THE VISCOSITY OF CERTAIN BLAST FURNACE SLAGS

CONTAINING TITANIA.

THESIS

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by

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C O N T E N T S.

INTRODUCTION.

The smelting of titania bearing iron ores has always been attended with considerable difficulty. During smelting most of the titania passes into the slag, rendering it sticky and very liable to form accretions of an infusible nature. Titanium carbo nitride (TiCN) and titanium nitride (TiN), have both been identified in these accretions; but the causes of the difficulty are still not completely understood. As a result of this, there has developed a considerable reluctance to use titaniferous iron ores, despite the considerable nature of the deposits existing in New Zealand and various other parts of the world.

This investigation was undertaken to elucidate the viscosity-temperature properties of some titania bearing blast furnace slags, in the hope of throwing some light on the smelting problem. Consequently the work was concerned primarily with quinternary lime-alumina-silica-magnesia-titania slags. It was considered worth while however, to take the opportunity presented, to gather a little further information concerning the viscosity of the simpler ternary (lime-alumina-silica) and quaternary (lime-alumina-silica-magnesia) slags. Consequently the work was started on a series of parent lime-alumina-silica slags, and from these, lime-alumina-silica-magnesia, and finally lime-alumina-silica-magnesia-titania slags were built up. By this means some information was obtained regarding the effects of magnesia and titania on slag viscosity.

Whether different minerals, such as calcium metasilicate, gehlenite etc., are wholly or only partly dissociated to their constitutent oxides in liquid slag, has long been a subject of controversy, and most of the physical properties normally studied - including viscosity - have been used to prove or disprove the beliefs of different workers. Consequently the results of the present work were carefully examined for positive or negative evidence on this problem. It is suggested that there are indications which would lead one to believe that some minerals at anyrate, are not wholly dissociated in the liquid state up to at least 1600°C.

Concurrently with the practical work outlined above, a study was made of the literature concerning the fundamental nature of viscosity, and its possible evaluation in terms of physical constants. The results of this study were rather surprising.

Although the physicists have a firmly established theory which adequately explains all the phenomena of gaseous viscosity, they have so far been remarkably unsuccessful in dealing with the problem of liquid viscosity. There is no accepted theory of the mechanism of viscous traction, and it is impossible to adequately answer such an apparently simple question, as why the viscosity of a liquid decreases with rise of temperature. It is not surprising, therefore, that very little is known concerning the laws governing liquid mixtures. This work

This work/ although very incomplete at the moment, will, when completely developed, be of considerable value to the technologist, and it was therefore considered essential to introduce a chapter which would give an idea of the progress so far achieved.

Meanwhile, until some of the fundamental problems of viscosity have been solved, the only method available to the metallurgist for investigating a problem such as that presented by titaniferous iron ores, is the systematic determination of viscosity, such as adopted in this paper.

Chapter I.

THEORY OF VISCOSITY OF LIQUIDS.

A fluid offers no permanent resistance to a force tending to change its shape, but yields steadily to the smallest deforming force. The rate of deformation by a given force does, however, vary from one fluid to another, and the property, viscosity, was introduced in order to evaluate the variation. Very extensive experiments have shown that the ratio of the shearing stress to the rate of shear is constant for any one liquid under constant temperature and pressure. This is the fundamental law of fluid friction, and the constant ratio of shearing stress in a fluid to its rate of shear is the coefficient of viscosity of that fluid.

When the coefficient is expressed in dynes, centimetres and seconds, then the unit of viscosity is called a poise, (in honour of Poiseuille). The hundredth part of a poise is called a centipoise, a unit which happens to approximate very closely to the viscosity of water at 20°C.

Fluidity (ϕ) is the reciprocal of viscosity (η), and is usually expressed as:-

$$\phi = \frac{1}{\eta \text{ (poise)}}$$

An adequate theory to explain the mechanism of viscosity and its variation with temperature and pressure, has not yet

has not yet/ been formulated. Probably the most promising so far proposed, is that due to Andrade.(1.2)

According to the accepted theory of viscosity of gases, energy is transferred from one layer to another, by the bodily transference of molecules through a distance large, compared with their own sizes. In the case of liquids, however, there is in the ordinary sense of the term, no mean free path, the motion of the molecules being always in an intense molecular field. It is therefore necessary to postulate another method of transference of energy from layer to layer.

Andrade assumes that this takes place by the temporary union of molecules of contiguous layers at the extremes of their vibrations. The time of this union is postulated to be no longer than that required for the molecules to acquire a common velocity of translation. The binding force, during this momentary association is the residual field of the molecules, which is sufficient to bind them permanently in the solid state, but is overcome by the energy of motion in the liquid state. As the temperature agitation in the liquid increases, the chances of a molecular union decreases, and the viscosity decreases, till finally the energy of motion exceeds the molecular energy of attraction, and the liquid boils.

For the transference of energy the molecules must possess a certain mutual negative potential energy E, and

energy E, and/ the viscosity will depend on the number of molecules possessing this energy at the extremes of their vibrations.

Then by the simplest application of the Boltzmann distribution function,

$$\eta = Ae^{b/T}.$$

where η is the viscosity at T° and A and b are constants.

Andrade[1.3] deduced from this theory that for simple monatomic liquids, the viscosity (η_{MP}) at the melting point (T_{MP}) should be given by :-

$$\eta_{MP} = K.\frac{(A\ T_{MP})^{\frac{1}{2}}}{V^{\frac{2}{3}}}$$

where A is molecular weight, V molecular volume at melting point and K is a constant of approximate value 5×10^{-4}.

The calculated results were of the correct order, and relative value for mercury, lead, tin, copper, antimony, bismuth, chlorine, bromine, iodine, oxygen and hydrogen.

More recently Andrade[4] has applied this formula to the monatomic liquids argon, potassium, caesium, tin, mercury, lead, copper, the fused salts of cubic structure sodium chloride, sodium bromide, potassium chloride, potassium bromide, and to the liquids of high molecular symmetry, carbon tetra chloride, methane and silicon tetrachloride.

As a result of this he has shown that:-

shown that/:-

$$\beta = \frac{\eta_{MP} V^{2/3}}{A. T_{mp}}$$

was approximately constant for molecules of given characteristic shape. These results give considerable credence to Andrade's theory of the mechanism of viscosity.

It is generally agreed that the viscosity-temperature equation which gives most satisfactory agreement with experimental data is :-

$$\eta = Ae^{b/T}$$

This was just proposed by de Guzman[5] as a result of a suggestion by Porter[6]. Since then, Dunn,[7] Sheppard,[8.9] Andrade[1.2] and Preston[10] have all arrived at the same equation by different methods. The true physical significance of A and b is never-:theless, still obscure.

According to Dunn[7], "b" may be identified as the quantity of energy necessary to impart to a molecule so that it may overcome the attraction of all its neighbours. Sheppard[9] suggests that "b" should be a work function involving the specific heat of the liquid, and proposes that it includes a term of the type $C_p (M d)^{2/3}$ where C_p is the specific heat, M the molecular weight and d the density. Andrade[11] on the other hand believes "b" to be $^1/_K{}^{th}$ (where K is the Boltzmann constant) of the total potential energy due to the intermolecular field. There is considerable disagreement, therefore, as to what constitutes the "critical energy" included in this term.

It is very probable that it will contain some power of the molecular weight. Pradsad[12] even suggests that variation of "b" with temperature can be used as a measure of degree of association, and points out that the method gives good agreement with other methods for the association factors of water.

Ward[13] and Nissen and Clark[14] believe that "b" is a function of temperature. In the case of associated liquids this is probable, but whether or not, there is a temperature factor apart from that associated with the molecular weight is still uncertain.

Even less can be said with certainty about the physical significance of the constant "A" in the formula:-

$$\eta = Ae^{b/T}.$$

Andrade[11] suggested that the term contained the factors $M^{3/2}\ d^{-1/3}$ where M is molecular weight and d density. Later, he introduced the equation:-

$$\eta = \frac{A'}{V^{1/3}} e^{c/VT}.$$

Since this a number of workers have suggested that "A" is a function of volume.

Eyring[15] suggested:-

$$\eta = \frac{Nh}{V} e^{E/KT}$$

and Sinha[16]

$$\eta = \frac{6RT}{nVv} e^{U/RT}.$$

The parochor is a measure of the molecular volume, and there is more precise data vaialable in the parochor form than as true molecular volume. Lewis[17] and Lewis and Morgan[18] have put forward viscosity-temperature formulae for groups of closely allied substances, in which A is a function of the logarithm of the parochor.

Apart from this rather vague relation to specific or molecular volume, little has been decided as to the true significance of A.

Frisch and Eyring[19] have recently derived a viscosity-temperature relationship in which the "A" term has assumed a very complex nature. They considered the mechanism of viscous flow as the passage over one another, of pairs of molecules in adjacent layers, and assumed this to be dependent on the laws governing the rearrangement of matter, by surmounting a potential barrier. On this assumption, viscosity and temperature are connected by the following equation:-

$$\eta = (\pi R T)^{1/2} N^{-1/3} \left(U_g / U_e V_1^{2/3}\right) e^{E/RT}.$$

R is the gas constant; N is the number of molecules in a given mass of liquid of volume V_1; U_g and U_e are the velocities of sound in the gas and liquid phases, while E is the "activation energy for viscous flow".

In the writer's opinion, Andrade's theory is superior to that of the earlier theory of McLeod, in view of its more fundamental approach to the problem. However, McLeod is the

McLeod is the/ only worker who has applied his theory with any success to the problem of the viscosity of liquid mixtures, it will therefore be convenient to outline his theory.

McLeod[20] assumed that viscosity depended on two factors, the "freespace", i.e. the total volume minus the volume occupied by the molecules, and the molecular weight. He suggested that viscosity decreased with increase of free space, and was greater, the greater the molecular weight.

For a non-associated liquid, or a liquid in which the degree of association does not alter over the range of temperature examined, the molecular weight is constant, and assuming the above we may write:-

$$\frac{\eta_o}{\eta_t} = \frac{(Xt)^A}{(Xo)}$$

where η_o is the viscosity at to°C and η_t the viscosity at t°C, while Xt and Xo are the corresponding "free spaces" at these temperatures, and A is a constant. McLeod assumed that free space followed the laws of simple expansion when pressure was constant thus:-

$$\frac{\eta_o}{\eta_t} = \left(\frac{Xo + \alpha t + \beta t^2 + \gamma + \ldots}{Xo}\right)^A$$

where α, β and γ are the normal coefficients of expansion for the liquid.

When this equation was fitted to experimental data, it was found that for non-associated liquids A had the approximate value of unity, but for associated liquids it

liquids it/ was larger. (e.g. for butyl alcohol it has the value of 3·4). This is explained by assuming that when a liquid is associating while cooling, the associated molecules enclose come of the "free space", and consequently the viscosity increases at a greater rate than for a non-associating liquid. Similarly, dissociation during heating, leads to an exceptional increase of free space and a rapid decrease of viscosity.

By plotting molecular weight against viscosity at temperatures of equal free space, McLeod[21] showed that there was reasonable ground for assuming viscosity proportional to molecular weight, or in the case of associated liquids, to the aggregate weight of the associated molecule. Thus he arrived at the formula:-

$$\eta = \frac{K(M^{\alpha})}{X}$$

where K is a constant; M the molecular weight, α an association factor and X the "free space".

In a later paper[22] he substitutes for the molecular weight, the exponential function $M_o e^{c_{11}/TV}$. giving the new equation.

$$\eta = \frac{K M_o e^{c_{11}/TV}}{X}$$

which he reduced to the form:-

$$\eta = \frac{B}{T} e^{c_{11}/TV}.$$

containing only two constants.

McLeod[23] assumes that the viscosity of mixtures, like that of pure liquids, was a function of free space. He suggested that the contraction in volume often exhibited by liquid mixtures, which show a maximum in their viscosity - composition curves, is the cause of the increased viscosity, and has the same effect as a contraction on cooling.

According to McLeod's theory[23] if two liquids are mixed, one of which has a low viscosity and therefore a large "free space" while the other has a high viscosity and a small "free space", the liquid with the large "free space" will shew some of it with the more viscous one.

In the development of this idea mathematically, McLeod was forced to adopt the approximation that the "free space" was the same for both components, and equal to ·100. The following equation for the viscosity of a mixture in terms of the viscosities of its constituents is therefore applicable only to mixtures or liquids of similar viscosity.

$$\eta = (\eta_1 V_1 + \eta_2 V_2) \left(\frac{\cdot 100}{(\cdot 100 - C)}\right)^{A_1 V_1 + A_2 V_2}$$

V_1 and V_2 are the volume fractions of liquids of viscosities η_1 and η_2; A_1 and A_2, are constants and C is the contraction on mixing per unit volume. As the value used for "free space" is an approximation, the constants A_1 and A_2 are quite different from those derived for the viscosity-temperature equation of the simple substance.

The above equation has been fitted to experimental data for some organic mixtures, with considerable success, and

considerable success, ~~and~~/ while with other mixtures it has failed. However, it is the most successful equation so far proposed, although it must be realised, that it, in its developement from McLeod's original theory, it has become largely ~~experience~~ empirical.

Clearly the physicist has many problems to solve before he will be able to calculate for the metallurgist, the viscosity of a furnace slag containing four, five, six or more constituents.

Chapter 2.

LITERATURE ON THE VISCOSITY OF BLAST FURNACE SLAGS.

More than 90% by weight of a blast furnace slag is made up of lime, alumina, silica and magnesia. The remainder, which in some cases may not exceed 3%, consists of calcium sulphide and traces of iron oxide, manganese oxide, titania etc.

The experimental study of the viscosity of blast furnace slags, consequently resolved itself into two parts:-

1. The systematic determination of the variation of viscosity with temperature and composition of lime-alumina-silica-magnesia slags in that part of the quaternary in which blast furnace slags normally occur.

2. The effect of small additions of other compounds such as calcium sulphide and iron, manganese and titanium oxides on the viscosity of the quaternary slags.

Binary Lime-Silica Melts.

The work done on the viscosity of simple lime-silica slags, has been largely a search for evidence of the existance of the compound calcium metasilicate ($CaO.SiO_2$) in the liquid state.

Endell[24.25] has published isothermal curves of viscosity against composition which show no break near the compound composition. The curves of Herty[26] and ~~of~~ his co-workers, and of Rait, McMillan and Hay[27], on the other hand, show a distinct minimum, almost exactly on the compound composition.

Consequently Endell asserts that calcium metasilicate is completely dissociated to its constituent oxides in binary lime-silica melts, while Herty and Rait both claim that the compound is at least partially stable at temperatures just exceeding its fusion point.

It is interesting to note that a similar state of affairs exists concerning the soda-silica system. Preston[28] claims the existence of a minimum in the isothermal viscosity curves corresponding to the compound $Na_2O.2SiO_2$; while Endell[24] and Lillie[29] claim that the curves are unbroken in the vicinity of the compound composition.

The results recorded in this paper supply further evidence that calcium metasilicate does exist in the liquid state.

Ternary Lime-Alumina-Silica Melts.

That portion of the lime-alumina-silica ternary of importance to blast furnace slags has been studied by Feild and Royster[30]; McCaffery[31]; and Rait, McMillan, and Hay.[27] In Fig.1, the results of the three sets of workers for a temperature of 1500°C are plotted as isovis curves on the same diagram. Clearly there is no correspondence in their results either in absolute values or in the general pattern of the curves. A comparison of results at other temperatures yields a similar lack of agreement.

Feild and Royster, and McCaffery both used Margule's apparatus, while Rait, McMillan and Hay used Searle's

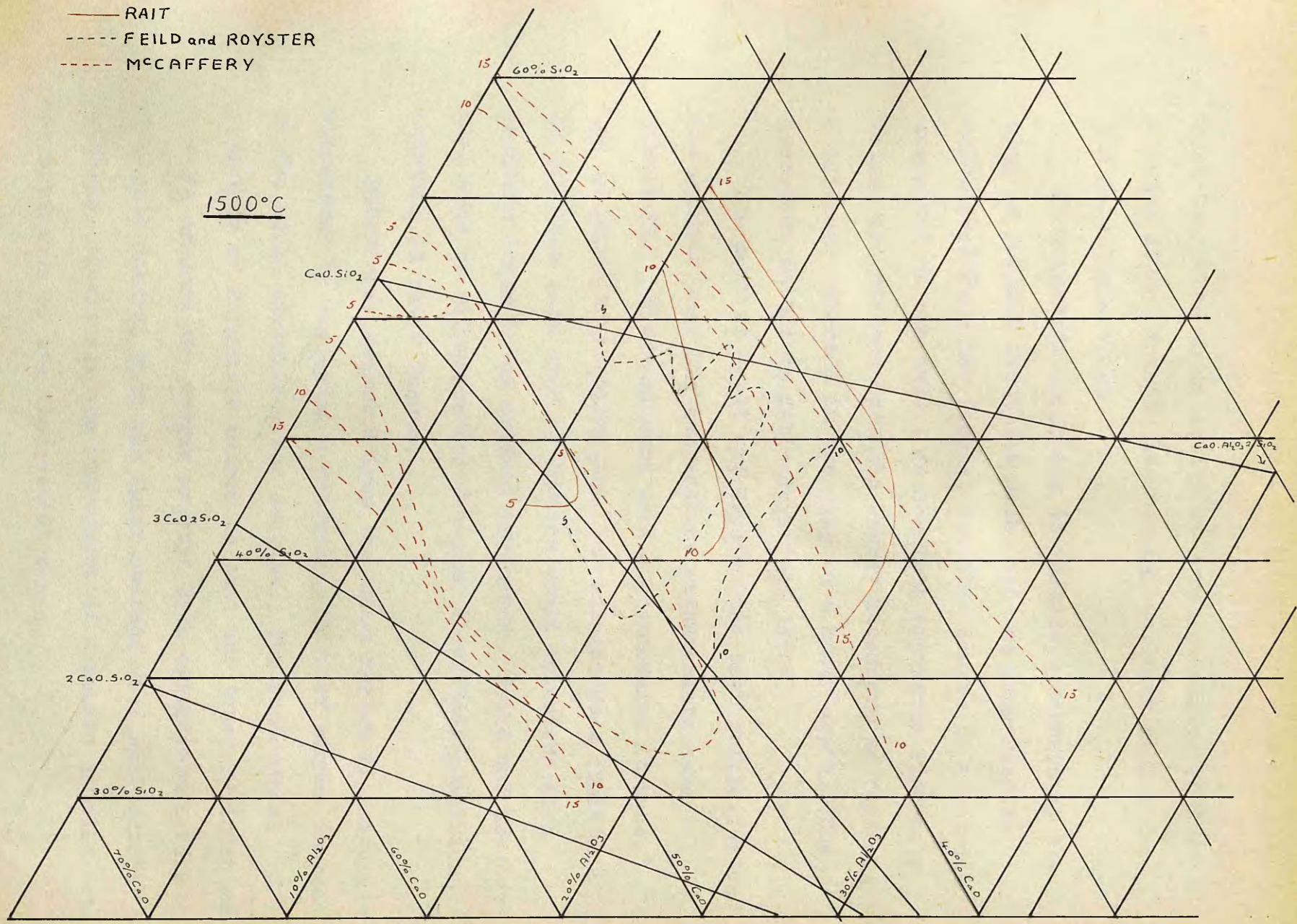
RAIT
FEILD and ROYSTER
McCAFFERY
1500°C
60% SiO2
CaO.SiO2
3CaO2SiO2
40% SiO2
2CaO.SiO2
30% SiO2
CaO.Al2O3.2SiO2
70% CaO
100% Al2O3
60% CaO
20% Al2O3
50% CaO
30% Al2O3
40% CaO

Figure 1

used Searle's/ modification of Margules apparatus for viscous slags, and the logarithmic decrement method for the more fluid slags.

In Margule's apparatus the crucible containing the slag is rotated about its axis, and the viscosity is calculated from the torgue, the slag exerts on a spindle suspended in the melt. In Searle's apparatus viscosity values are deduced from the energy necessary to rotate a a cylinder immersed in the slag to a known depth. The decrement method is fully described later.

The work of Feild and Royster has been criticised on the grounds that his temperature measurements were unreliable. These workers used a granannular furnace, and as McCafferey points out, the considerable evolution of gas from this type of furnace would interfere with readings taken by an optical pyrometer. Feild and Royster also made no allowance for the non black body conditions existing in their furnace.

McCafferey departed from the usual design of Margule's viscometer by employing a central spindle of square instead of the usual circular cross section. The fundamental principle of Margule's method is that the inner cylinder be used to measure the torgue exerted by a cylinderical film of liquid coaxial with the inner surface of a cylindrical crucible. Obviously the employment of a square spindle robs the apparatus of its theoretical basis.

McCafferey did not use his apparatus as an absolute instrument, but calibrated it against a liquid of known viscosity (castor oil). Even this, does not put his apparatus on a physically sound basis, for there is bound to be turbulent flow around a square spindle, owing to the variation of the width of the channel, through which the liquid must flow. This will be especially so at the edges of the square, where the liquid has suddenly to change its direction through a right angle.

McCafferey adopted this shape of spindle because it gave greater deflections than the cylindrical type. It is probable that the increase of deflection is due to turbulent flow, and is a function of slag density.

Clearly McCaffery's results are to be accepted with reserve.

The most reliable study of the viscosity of lime-alumina-silica slags at present available, is that due to Rait, Hay and McMillan. As mentioned above, these workers used Searle's apparatus for the more viscous slags and the logarithmic decrement for the more fluid. Both of these methods are based on a reliable theoretical basis. Temperature measurements were made with a tungsten-molybdenum thermocouple, and are not therefore open to the criticisms levelled at the work of Feild and Royster. In this connection, it may be noted that Rait et al, got inflexions in their viscosity-temperature curves, corresponding to the liquidus

the liquidus/ temperature, which were in close agreement with temperatures given by Rankin and Wright.[39]

Quaternary Lime-Alumina-Silica-Magnesia Melts.

The only systematic examination of the viscosity-temp-:erature relations of lime-alumina-silica-magnesia slags is due to McCaffery et al.[31] The method employed by these workers has already been discussed. Their results led them to two important conclusions.

1. The addition of magnesia to a lime-alumina-silica slag decreases the viscosity donsiderably.

2. The effect of varying the lime, alumina or silica contents of a quaternary slag does not alter the viscosity at a given temperature, so greatly, as would a corresponding alteration in a simple ternary slag.

The Effect of small Amounts of other constituents on the Viscosity of Quaternary Slags.

The work on what was described in the opening paragraph as the second part of the study of the viscosity of blast furnace slags, is at the moment very fragmentary and incomplete.

Both Tsylev[32] and Semik[33] agree that small percentages of manganese oxide decrease the viscosity of quaternary slags. They disagree, however, as to the effect of calcium sulphide. Tsylev states that small additions of Calcium sulphide increase the viscosity of lime-alumina-silica-magnesia slags, the effect being greatest in the more basic slags. Semik's

Semik's/ results suggest that although calcium sulphide increases the viscosity of the more acid quaternary slags, the effect on the more basic is, if anything, to decrease the viscosity.

Endell and Kley[34] have studied the effect of small additions of potash, soda and ferrous oxide to quaternary slags and found that they all decrease the viscosity, ferrous oxide being the most and potash the least effective.

With the exception of a few isolated determinations by Endell and Brinkmann[35] and Volarovich[36] there has been no attempt to study the effect of titania on the viscosity of blast furnace slags.

Chapter 3.

The LOGARITHMIC DECREMENT METHOD OF MEASURING VISCOSITY.

It was decided to use the logarithmic decrement method of measuring viscosity. This was first introduced by Coulomb[37], who caused a horizontal circular disc suspended from a wire, to oscillate about its axis, in air, and then in the liquid to be examined. From the logarithmic decrement of the discs motion he deduced certain "resistance factors", but made no attempt to derive absolute viscosities.

The method was first used at high temperatures by Endell[24], who used an oscillating body which consisted of a platinum ball at the end of a short platinum rod. He calibrated his apparatus against liquids of known viscosity and used it to investigate soda-silica melts.

The form of oscillater used in this paper was introduced by Rait and Hay[38]. In their investigation of the viscosity of lime-alumina-silica slags, these workers used an oscillater which consisted of a long rigid spindle, suspended from a phosphor bronze suspension tape. The immersed part of the spindle was cylindrical in shape. This form has a no less secure theoretical foundation, and is much more convenient to work with in the limited space available in a high temperature furnace, than either of the two forms mentioned above.

The apparatus used by Rait and Hay had a useful range

a useful range/ of 0·5 - 16 poise. This has been increased to 0·5 - 40·0 poise in the present apparatus by replacing the phospher-bronze suspension by a steel suspension of greater restoring torque.

Theory of the Decrement Method.

When the spindle is oscillating with the cylinder immersed in the molten slag, the acceleration at any instant is controlled by two forces; the restoring torque of the suspension and the damping action of the slag. If the torque per unit twist of the tape be D, then when the spindle is X degrees from its zero position, the restoring torque will be - D X. The damping action of the slag is proportional to its viscosity and to the velocity of the cylinder surface, and will be $-K\eta\frac{dx}{dt}$ where η is the viscosity, and K an apparatus constant.

The motion of the cylinder can then be represented by the following equation;-

$$I\frac{d^2x}{dt^2} = -K\eta\frac{dx}{dt} - Dx$$

where I is the moment of inertia, of the spindle about its axis of rotation. The solution of this equation, assuming that the spindle starts from rest, with an original amplitude a. at time zero is:-

$$X = \frac{a\sqrt{D/I}}{\sqrt{\left[D/I - (K/2I)^2\right]}}\, e^{\frac{-K\eta t}{2I}} \cos\left[\sqrt{\left(\frac{D}{I} - \left(\frac{K}{2I}\right)^2\right)}\, t - \phi\right]$$

where, $\tan\phi = \dfrac{K\eta/2I}{\sqrt{\left[D/I - (K/2I)^2\right]}}$

This solution can be written as:-

$$X = C\, e^{-K\eta t/2I} \cdot \cos\left[\sqrt{\left(\frac{D}{I} - \left(\frac{K}{2I}\right)^2\right)}\, t - \phi\right]$$

where $$C = \frac{a\sqrt{D/I}}{\sqrt{\left[D/I - (K\eta/2I)^2\right]}}$$

Thus the period of oscillation T, is given by:-

$$T = \frac{2\pi}{\sqrt{\left[D/I - \left(\frac{K\eta}{2I}\right)^2\right]}}$$

The damping factor of the motion is $Ce^{-k\,t/2I}$ and therefore at time t the amplitude is:-

$$a_1 = C\, e^{-k\eta t/2I}.$$

and at time t and T:-

$$a_2 = C\, e^{-k\eta(t + T)/2I}$$

Thus the logarithmic decrement $\log_e p$, is

$$\log_e p = \log_e \frac{a_1}{a_2} = \frac{K\,T}{2\,I}$$

Substituting for T and solving for η.

$$\eta = \frac{\sqrt{DI}\,\log_e p.}{K\pi\sqrt{\left[1 + \frac{(\log_e p)^2}{4\,\pi^2}\right]}}$$

$$\doteq \frac{\sqrt{DI}\,\log_e p.}{K\,\pi} \quad \text{when } \log_e p \text{ is very small.}$$

Thus for small decrements the viscosity is directly proportional to the logarithmic decrement. This was verified experimentally by Rait and Hay.(38)

Chapter 4.

DESCRIPTION OF APPARATUS EMPLOYED.

Scale diagrams of the apparatus are given in Figs. 2 and 3.

The furnace was of the resistance type, the heating element consisting of 36 feet of ·04 inch diameter molybdenum wire wound five times to the inch on a three inch diameter alundum former.

The oscillating part or spindle of the viscometer was suspended from a brass gibbet by a steel suspension tape. The asbestos platform to which this gibbet was fixed, rested on a rectangular framework built up from the furnace casing, and could be accurately levelled by four of the usual screw devices.

The horizontal arm of the gibbet could be raised or lowered through a distance of three inches. This was a coarse adjustment only, a fine adjustment by means of which the spindle could be raised or lowered by small exact amounts being incorporated immediately above the suspension tape. The fine adjustment was provided with a pointer which moved over a small scale graduated in tenths of an inch.

The upper part of the spindle was of brass and consisted of a vertical rod and cross beam. The latter carried two symmetrically placed 100 gm. weights, which supplied

Keys to Figs. 2 and 3.

1. Furnace feet.
2. Furnace legs.
3. Inlet for protecting gases.
4. Pythagoras tube.
5. Furnace casing.
6. Furnace winding.
7. Graphite crucible.
8. Graphite inner oscillating cylinder.
9. Graphite rod.
10. Graphite coupling.
11. Graphite rod.
12. Duralumin coupling.
13. Brass rod.
14. Pythagoras tube.
15. Brass crossbar and 100 gm. weights.
16. Lower clamp for steel suspension.
17. Steel suspension.
18. Upper clamp for steel suspension.
19. Fine adjustment for spindle.
20. Furnace tie-rods.
21. Crossbar of gibbet.
22. Vertical pillar of gibbet.
23. Asbestos platform.
24. Framework supporting viscometer.
25. Outer alundum sleeve of furnace.

26. Levelling screws for asbestos platform.

27. Tungsten-molybdenum thermocouple.

28. Alundum stool supporting crucible.

29. Furnace leads.

30. Clamp for coarse adjustment of spindle height.

31. Rubber bung.

32. Asbestos packing.

33. Aluminium pointer.

34. Scale.

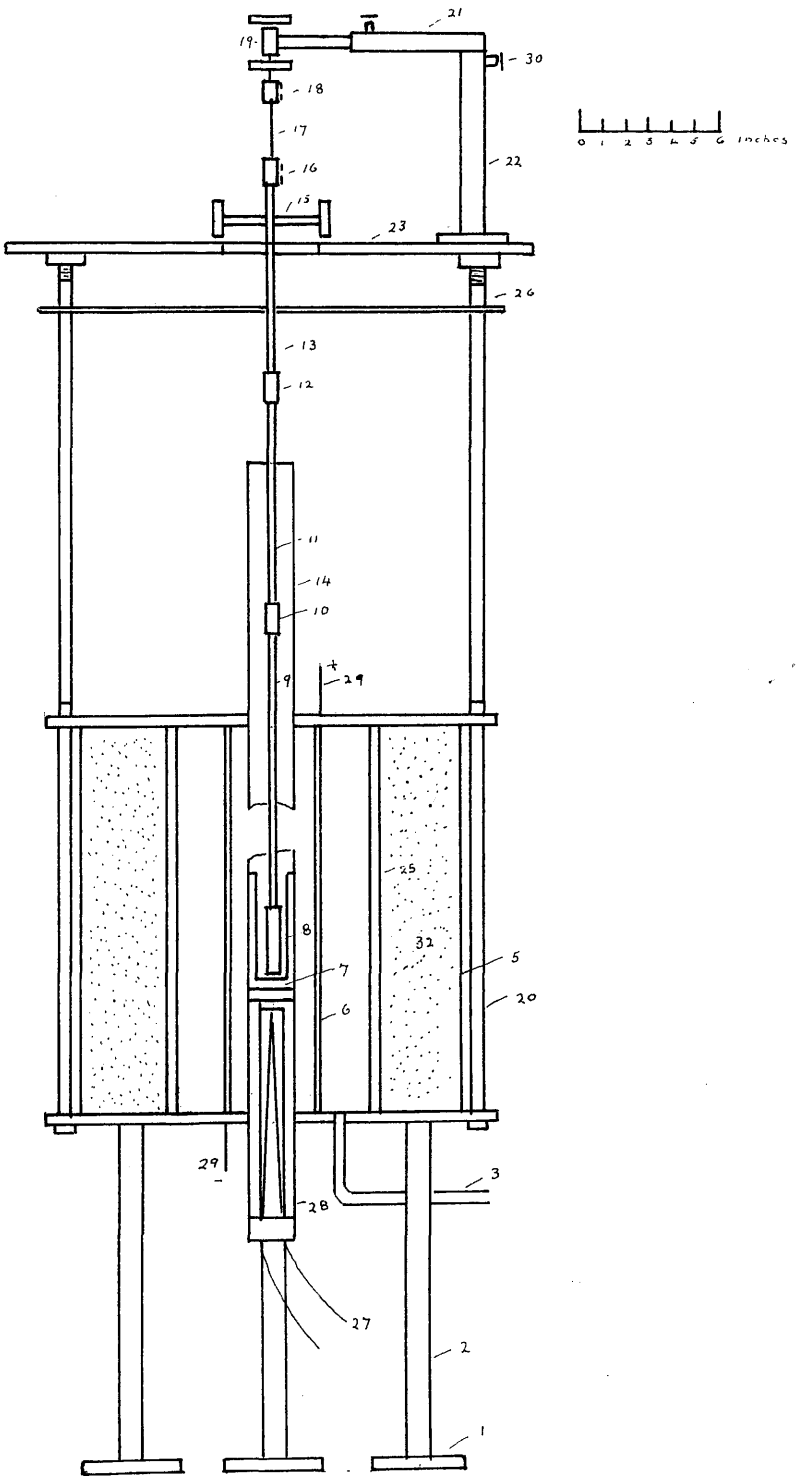
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Figure 2

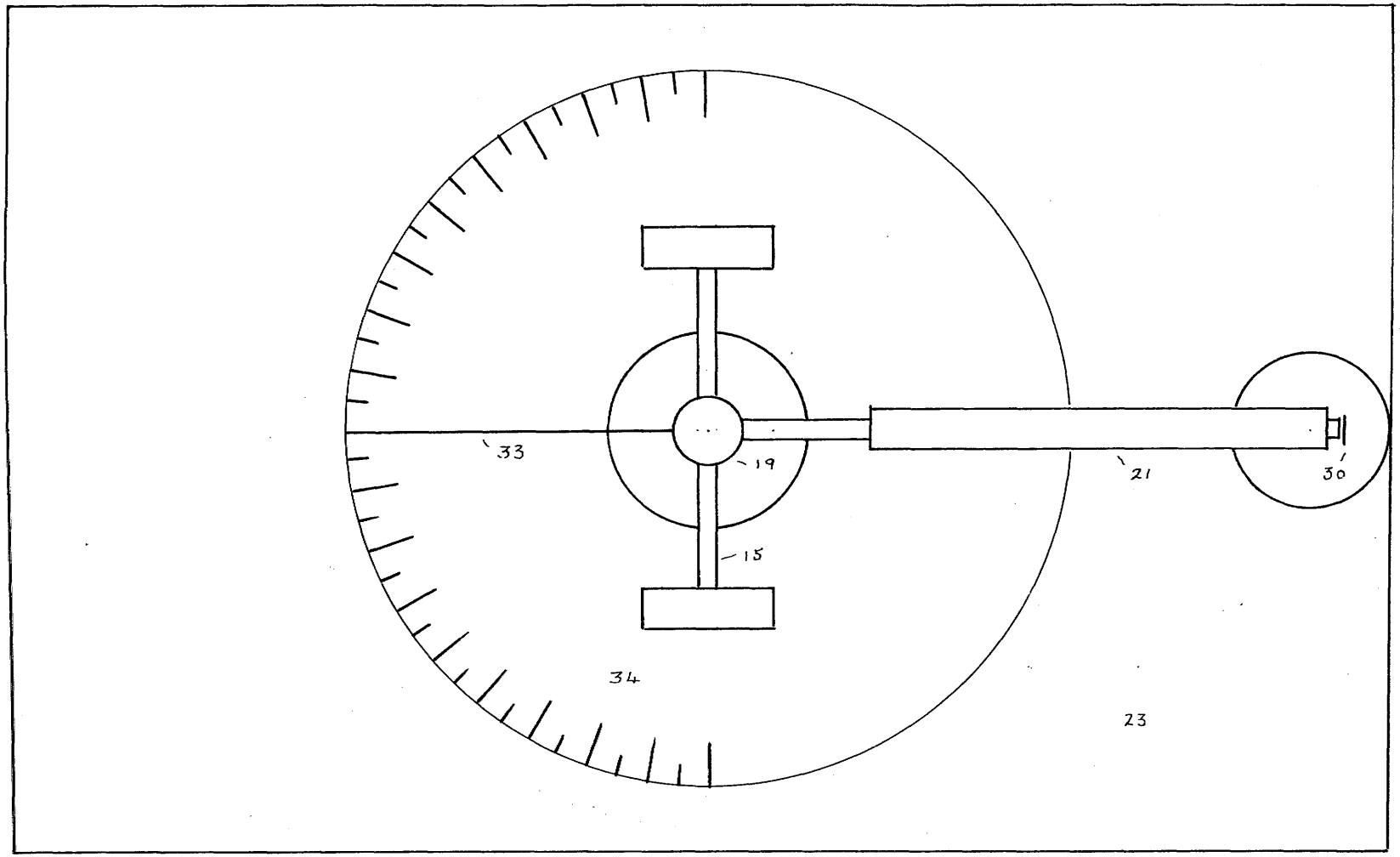


Figure 3

which supplied/ stability to the rotation of the apparatus. By varying the position of these weights on the cross beam, the moment of inertia of the rotating system could be altered, and hence the viscosity range of the apparatus varied. It was not found necessary, however, to make use of this variable. With the weights kept at a constant distance apart of 2·50 inches, the apparatus was accurate and sensitive, over the range 0·5 - 40 poise. This was found to be ample for the viscosity values encountered.

An adjustable aluminium pointer was clipped in a horizontal position, to the vertical rod of this part of the spindle. When the spindle was oscillating, this moved over a circular scale graduated in degrees on a polished sheet of metal, screwed to the asbestos platform.

The upper part of the spindle was connected to the lower refractory part by a duralumin coupling.

The choice of refractory for the crucible, and the lower part of the spindle was very limited, since few materials are able to withstand both slag corrosion and the high temperatures involved. It was decided to use graphite in view of its ready availability, and its ease of machining to accurate dimensions. A disadvantage of graphite was that it could not be used in an oxidising atmosphere. The molybdenum furnace winding, however, also required protection from oxidation, and it was therefore a simple matter to arrange the apparatus so that the same

the same/ stream of gases protected both the furnace winding and the graphite parts of the viscometer.

The protecting gases were prepared as follows:-

Liquid ammonia (sg. 0·88) was heated in a flask over a bunsen burner. The ammonia gas thus obtained was cracked to a mixture of nitrogen and hydrogen by passing over red hot steel turnings. Any residual ammonia in the cracked gas was washed out by bubbling through water and then dilute sulphuric acid. The gases were dried by concentrated sulphuric acid, and calcium chloride, before passing into the furnace. This section of the apparatus is shown in Fig. 4.

The long graphite rod extending from the duralumin coupling down to the inner rotating cylinder, was, for the sake of economy, made up of two lengths of graphite rod joined by a graphite coupling. The lower part was at a temperature of over 1400°C for long periods, and was slowly burned away by traces of oxygen which unavoidably entered the apparatus. This part had consequently to be periodically replaced. The wear on the inner cylinder, which of course, was completely immersed in the slag, was negligible. The only effect of constant use was to render the graphite brittle

The crucibles and inner rotating cylinders were machined to the following dimensions.

Crucible

Internal diam. 1·5 inches.

Key to Fig. 4.

A - Flask of 0·88 ammonia heated by Bunsen burner.

B - Mercury safety-valve.

C - Trap to catch liquid distilling over from A.

D - Furnace containing tubes in which steel turnings are heated to red heat.

E - Safety trap.

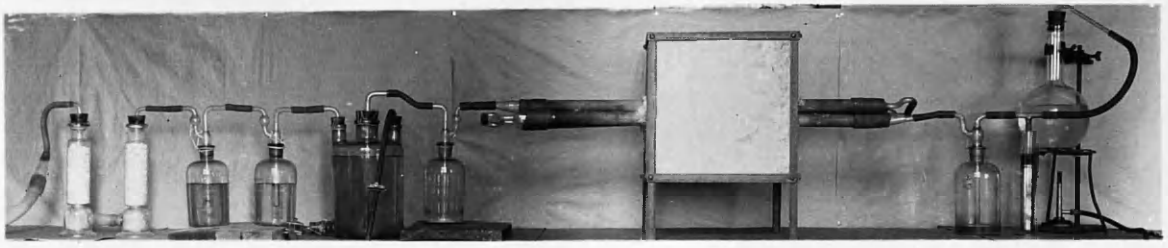
F - Wash-bottle containing water.

G - Wash-bottle containing dilute sulphuric acid.

H - Wash-bottle containing concentrated sulphuric acid.

I and J - Drying towers containing calcium chloride

K - Rubber tube leading to furnace.



K J I H G F E D C B A

Figure 4.

External diam. 1·9 inches.

Internal height 5 "

External height 5·3 "

Inner Cylinder.

Diameter 0·5 inches.

Length 2·0 "

Temperature Measurement.

Slag temperatures were determined by a tungsten-molybdenum thermocouple, using a Tinsley vernier potentiometer to measure the e.m.f. developed. This couple was used rather than the more usual platinum -platinum rhodium, because the reducing conditions prevailing in the furnace would have rapidly enbrittled platinum.

The tungsten-molybdenum couple can not be used in an oxidising atmosphere, and the melting points of the usual standardising metals are affected by a reducing atmosphere. It was therefore necessary to carry out the calibration of the couple in vacus.

Over the lower temperature range (15 - 1000°C), the couple was calibrated against a previously standardised chromel-alumel thermocouple. For the higher temperature range (900 -1600°C), the bridge method of Adcock, was employed, using fine wires of gold, silver and platinum, as standards.

The calibration curve is reproduced in Fig. 5.

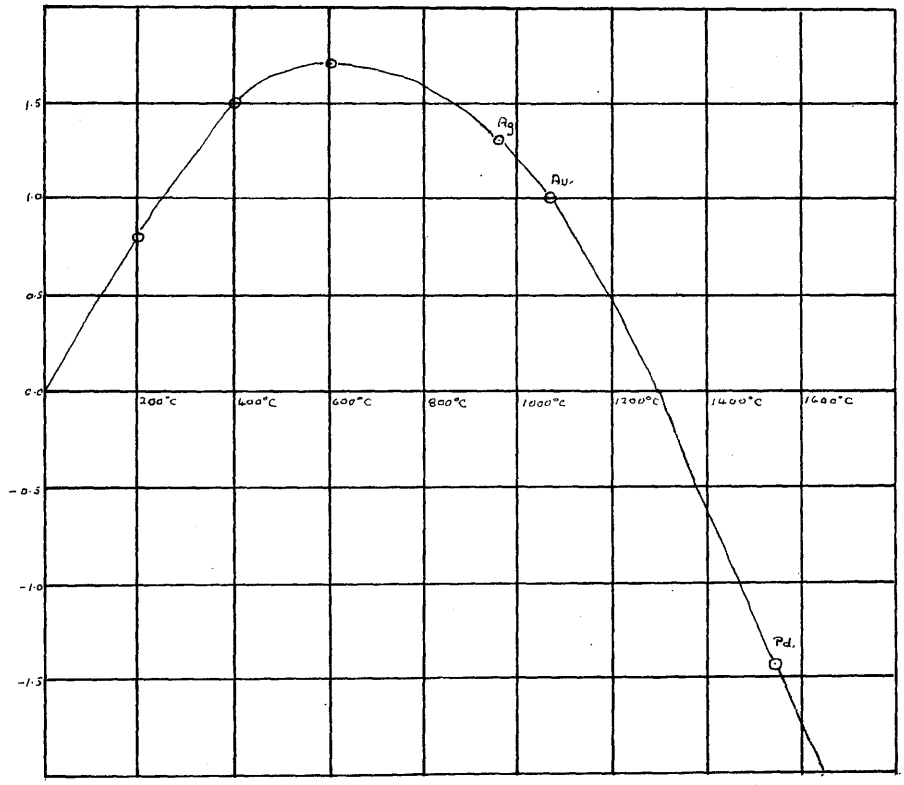

1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
200°C
400°C
600°C
800°C
1000°C
1200°C
1400°C
1600°C
Ag
Au
Pd

Figure 5

Owing to the sensitivity of viscosity to small temperature variations, certain precautions were taken to ensure that correct temperatures were recorded. Before the sizes of the crucible and inner spindle had been decided upon the furnace tube was explored with a thermocouple to find the temperature variation over its length. The dimensions of the crucible and inner cylinder were then fixed, so that the part of the crucible containing the slag and the couple point, were well within the zone of uniform temperature.

The couple point during viscosity determinatins was immediately under the centre of the crucible base. The couple was placed here, rather than somewhere on the crucible wall, because owing to the rapid fall of the angular velocity of the liquid from the inner cylinder to the crucible wall, the effect of the central column of the liquid predominates in the resultant decrement of the cylinder's motion. It is therefore more accurate to measure the temperature at the centre of the crucible, and thus minimise the effect of any possible transverse gradient.

Owing to the large mass of slag used (200 gm.), it naturally took considerable time for the crucible and its contents to acquire a uniform temperature. To ensure this uniform state had been attained, the furnace was held at the desired temperature for 20 mins.before readings were taken.

Chapter 5.

CALIBRATION OF APPARATUS.

The apparatus was standardised against liquids of known viscosity. Those used were:-

Castor oil at 15°C ---- 15·14 poise.

Castor oil at 20°C ---- 9·86 poise.

Viscous oil at 20°C --- 24·6 poise.

The viscosity values for castor oil were taken from the International Critical Tables. The figure for the viscous oil was obtained experimentally, using an Ostwald viscometer, which had been standardised against castor oil.

It was found convenient to perform the standardisation away from the furnace. The arrangement used is indicated in Fig. 6.

The crucible was filled to the standard level of 3·0 inches with the standardising liquid. The position of the spindle was then adjusted so that it was co-axial with the crucible and exactly 0·2 inches above the bottom of the crucible. This latter adjustment was most conveniently attained by lowering the spindle until it just touched the crucible bottom and then raising it through exactly 0·2 inches by means of the fine adjustment.

The temperature of the liquid in the crucible was controlled by adjusting the temperature of water flowing through the hollow brass container, within which the crucible

KEY TO FIGURE 6.

1. Viscometer Spindle.
2. Crucible.
3. Water Jacket.
4. Electrically driven Pump.

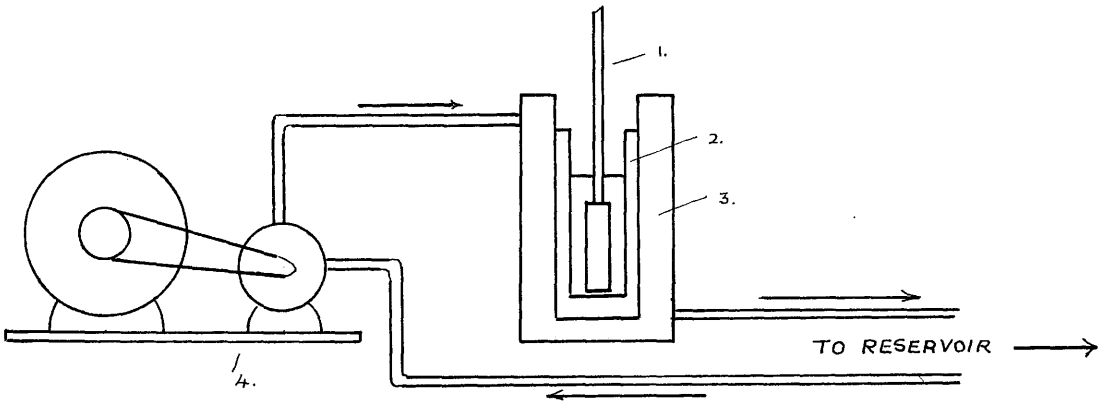


Figure 6

the crucible/ rested. This water was circulated from a thermostatically controlled tank, through the container, and back to the tank by means of a small electric pump.

The temperature of the liquid in the crucible was determined by a mercury thermometer graduated in tenths of a degree.

When the temperature had been correctly adjusted, the spindle was set in rotation and the logarithmic decrement of the motion determined. As indicated in the discussion of the theory of the method, the logarthimic decrement is the natural logarithm of the ratio of successive amplitudes of the spindles oscillations. When the damping action of the slag is slight, i.e. when the slag is fluid, it is more accurate to note the amplitude of the first oscillation a_1, and of the nth oscillation a_n, then the logarithmic decrement is $^1/_n \log_e {}^{a_1}/_{an}$.

A number of decrement values was obtained for each of the three standardising liquids,and the averages plotted against the corresponding viscosity value. The calibration curves obtained for three different suspension tapes are reproduced in Fig. 7. Nos. 2 and 3 were taken from the same steel spring, while No. 1. was taken from a batch of considerably higher restoring torque.

The viscosity - temperature relationships of a number of lime-alumina-silica slags, lying within the range previously examined by Rait, McMillan and Hay were investigated.

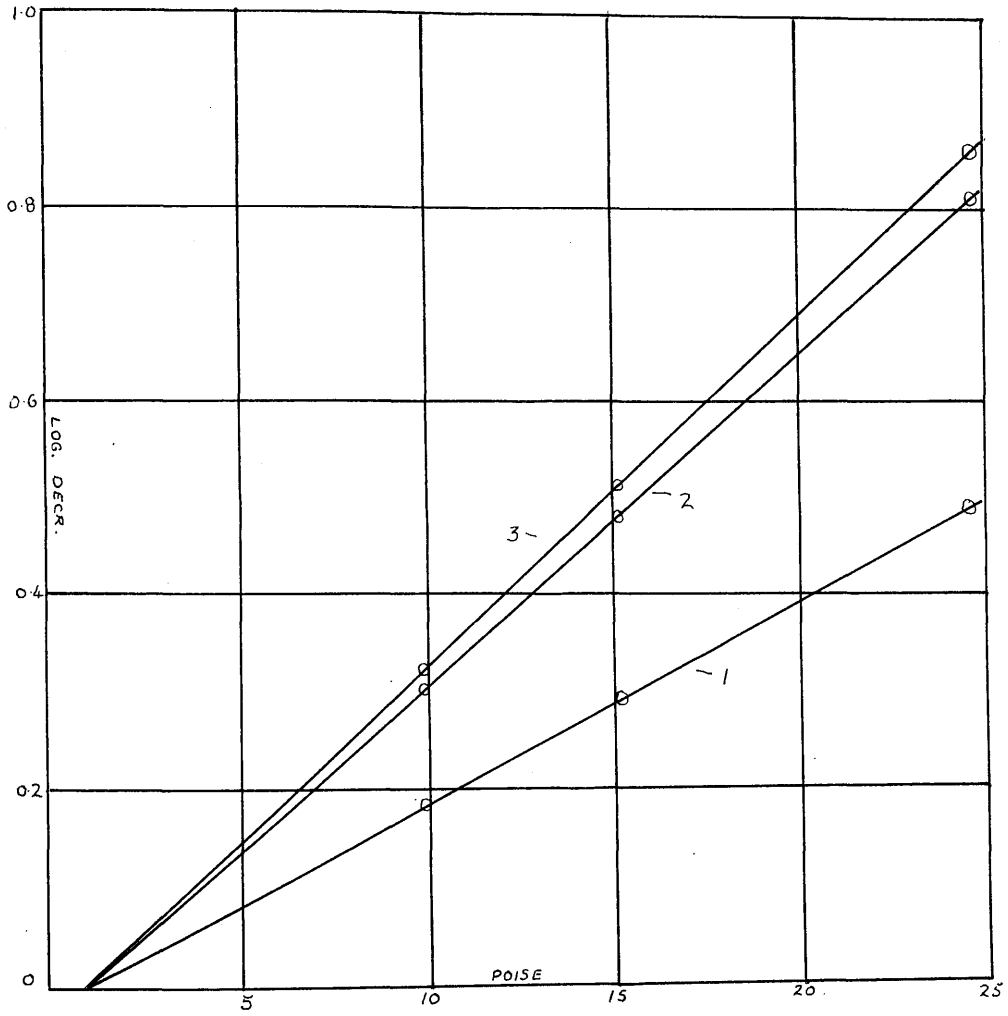


Figure 7.

This supplies a valuable check on the calibration. The detailed results of a typical viscosity - temperature curve are shown in Table 1. The agreement within the different sets of logarithmic decrement values can be taken as representative of that normally obtained. Composition 39·5% CaO, 49·4% SiO_2, 11·1% Al_2O_3 by weight.

Temp. °C	Logarithmic Decrement. 1	2	3	4	5	Average	Calbn. Const.	Viscosity. poise.
1450	·27	·27	·265	·265	·265	·267	50·6	13·5
1500	·18	·18	·18	·175	·175	·178	50·6	9·0
1550	·12	·12	·11	·11	·115	·115	50·6	5·8
1600	·067	·060	·062	·061	·065	·063	50·6	3·2

Table 1.

The results obtained for this series of ternary slags, are compared with those of Rait et. al. in Table 2.

No.	Composition - wt.%. CaO.	SiO_2	Al_2O_3	Viscosity in poise at:- 1450°C	1500°C	1550°C	1600°C
1	39·5	49·4	11·1	13·5(12)	9·0(9)	5·8(6)	3·2(3)
2	42·1	46·8	11·1	11·1(10)	7·1(7)	4·6(4·5)	2·8(2)
3	44·5	44·5	11·1	9·0(9)	5·5(6)	3·9(3·5)	3·3(2·5)
4	46·5	42·4	11·1	-(10·5)	5·8(5·5)	4·2(4·0)	3·3(3)

Table 2.

The figures in parenthesis are extrapolated from Rait's results[4] and can therefore be given only to the nearest 0·5 poise.

The agreement is satisfactory, and it can therefore be stated that the viscosity figures given in this paper are strictly relative to those given in previous papers issued from this Department.

In all, five suspensions were used to obtain the results reported. As indicated above, three of these were calibrated against liquids of known viscosity, and then checked against lime-alumina-silica slags. The remaining two were calibrated directly against slag 1, of Table 2.

Chapter 6.

EXPERIMENTAL PROCEDURE.

All slags were prepared synthetically. The chemicals used were of the grade which is sold commercially as "pure". With the exception of the lime, the constituents were weighed out in the oxide form. The lime was weighed out as calcium carbonate, and separately ignited to calcium oxide in a gas muffle. The thoroughly mixed oxides were packed into a crucible and melted out in the furnace. The resultant slag was held at 1600°C, for not less than half an hour before any viscosity determinations were attempted.

The first few minutes of this period were utilised to manoeuvre the spindle into its standard position in the melt. By means of the coarse adjustment, the spindle was slowly lowered through the slag, till it just touched the crucible bottom. This point was easily discernible by the sudden sagging of the suspension tape. The fine adjustment was then used to raise the spindle till it was exactly 0·2 inches clear of the crucible. If necessary adjustments were then made to bring it exactly into the centre of the crucible.

The spindle was now swinging freely with the inner cylinder completely immersed in the slag. It was allowed to come to rest and the zero reading of the pointer noted.

To take readings, the spindle was set in motion, care

care/ being taken to ensure that all the motion was about the axis of the spindle. Consecutive readings were then taken of the extreme positions of each swing of the pointer on one side of the zero. From these readings the logarithmic decrement of the motion was calculated as described previously. The procedure was repeated until several results in close agreement had been obtained.

Readings were subsequently taken at 1550°C, 1500°C, etc. until the slag solidified. The slag was held for 20 minutes at each temperature before a reading was taken.

After a satisfactory vicosity - temperature curve had been obtained, the composition of the slag in the crucible was altered by making additions of known weights of magnesia, titania or alumina. This was thoroughly mixed into the slag by using the spindle as a stirrer, and the viscosity - temperature curve corresponding to the new composition determined exactly as before.

The error introduced by this method was not great, owing to the fact that the initial charge of 200 gm. when melted out was always of sufficient volume to completely immerse the inner cylinder. Thus the effect of the addition was merely to slightly increase the length of the comparatively narrow spindle stem immersed in the slag.

In no case did the total addition made to a single charge exceed 10 gm. When this figure had been searched,

been searched, the crucible and its contents were discarded and the series continued by making up a fresh charge of 200 gms. of the new composition.

Chapter 7.

DISCUSSION OF RESULTS.

(1) Lime-Alumina-Silica Slags.

Six slags from the lime-alumina-silica ternary system were examined. These all contained 11·1% alumina, while the lime content varied from 39·5 - 50·3%. The chemical compositions are given in Table 3, together with the viscosity coefficients for 1450, 1500, 1550 and 1600°C.

No.	$\frac{CaO}{SiO_2}$	Composition - wt.%			Viscosity in poise at:-			
		CaO	SiO_2	Al_2O_3	1450°C	1500°C	1550°C	1600°C
1.	0·8	39·5	49·4	11·1	13·5	9·0	5·8	3·2
2.	0·9	42·1	46·8	11·1	11·1	6·4	5·1	4·0
3.	1·0	44·5	44·5	11·1	9·0	5·5	3·9	3·3
4.	1·1	46·5	42·4	11·1	-	5·8	4·2	3·3
5.	1·2	48·6	40·3	11·1	-	7·0	5·0	4·1
6.	1·3	50·3	38·6	11·1	-	6·6	5·0	4·8

Table 3.

The above figures are plotted as isothermal curves of viscosity against composition in Fig. 8.

The phase constitution of these slags in the solid state can be obtained from Fig. 9, which shows part of the lime-alumina-silica phase diagram. The range covered by the six slags is indicated by a dotted line. The series starts very near the calcium metasilicate-anorthite binary, crosses the calcium metasilicate - gehlenite binary at

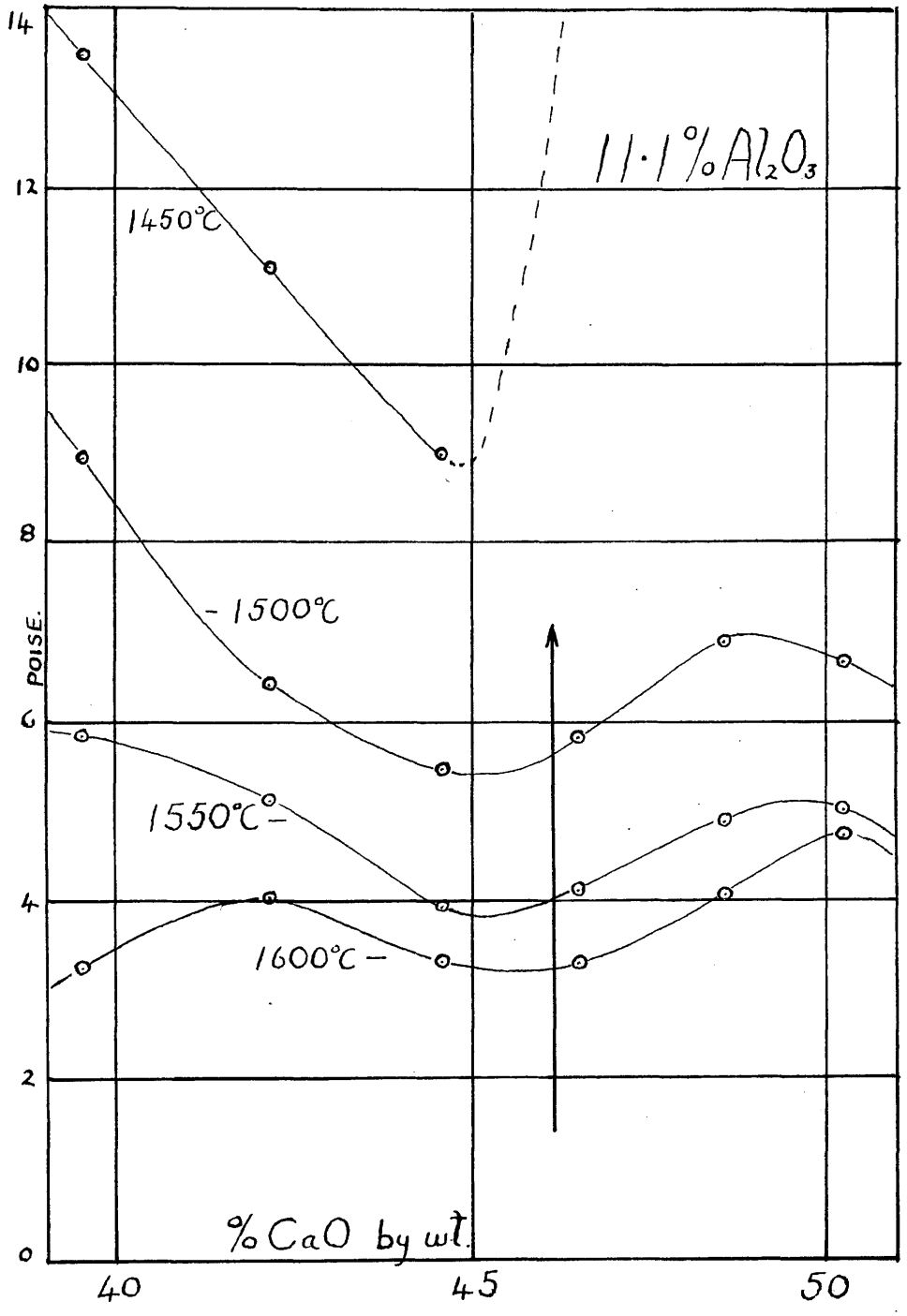

14
12
10
8
6
4
2
0
POISE.
11·1% Al_2O_3
1450°C
1500°C
1550°C
1600°C
% CaO by wt.
40
45
50

Figure 8.

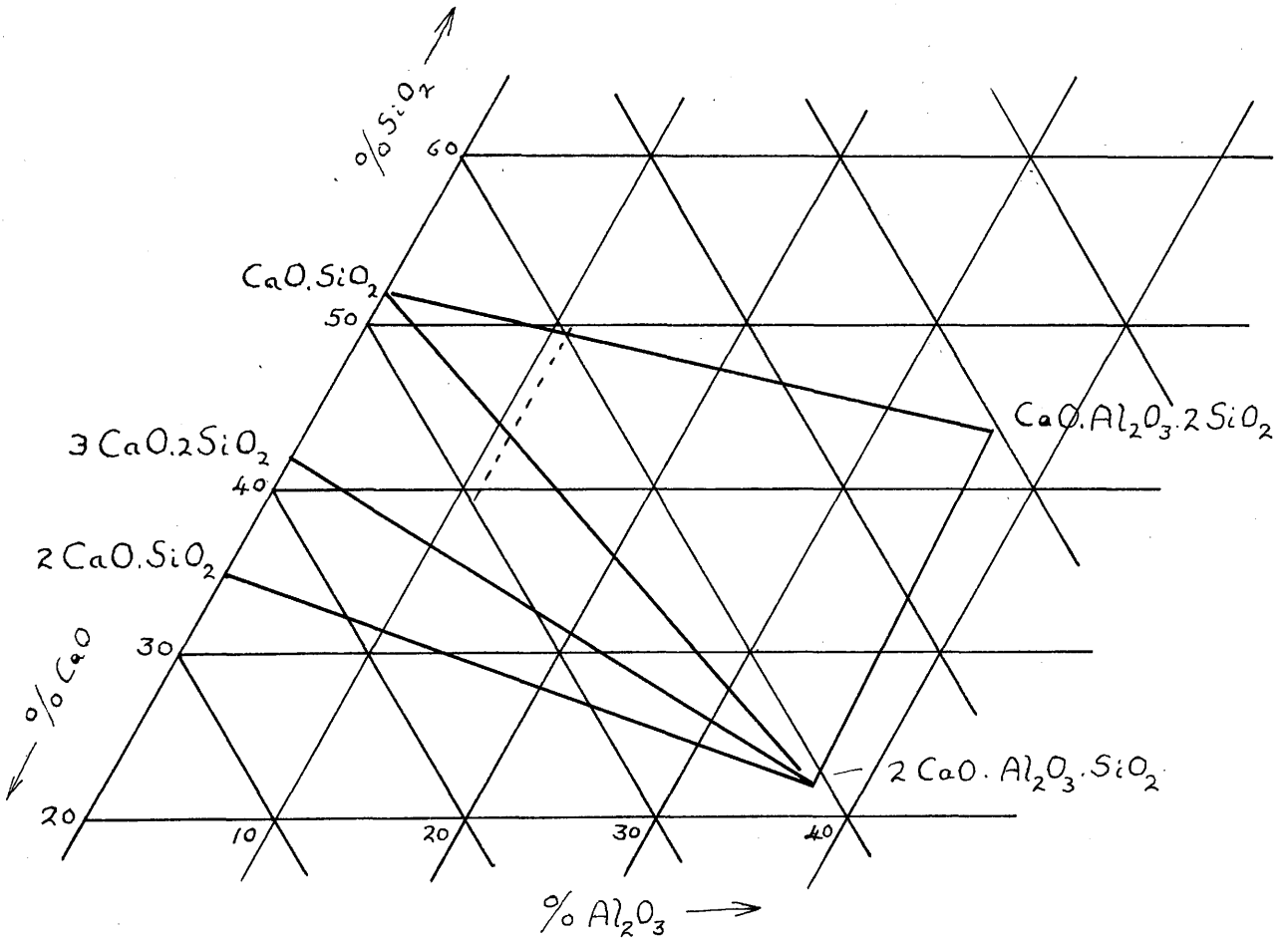

% SiO2
60
CaO.SiO2
50
CaO.Al2O3.2SiO2
3CaO.2SiO2
40
2CaO.SiO2
% CaO
30
2CaO.Al2O3.SiO2
20
10
20
30
40
% Al2O3

Figure 9.

binary at/ approximately 46% lime, and finishes halfway across the calcium metasilicate - gehlenite - calcium sesquisilicate ternary. The position of the calcium metasilicate-gehlenite line is indicated on the isothermal viscosity curves by an arrow. (Fig. 8).

The composition of the point of intersection with the binary line, and the composition of the minimum point shown by all four of the isothermal viscosity curves differ by only 0·5% lime. Rait, Hay and McMillan, have shown that a similar coincidence of the viscosity minimum with the gehlenite-calcium metasilicate binary persists up to at least 15% alumina.

(2) Lime-Alumina-Silica-Magnesia Slags.

Eight slags of the quaternary system lime-alumina-silica-magnesia were examined. These all contained 10·5% alumina, and 5·3% magnesia. The chemical compositions are given in Table 4, together with the viscosity coefficients for 1450, 1500, 1550 and 1600°C.

No.	$\frac{CaO}{SiO_2}$	Composition - wt.%				Viscosity in poise at:-			
		CaO	Al_2O_3	SiO_2	MgO	1450°C	1500°C	1550°C	1600°C
1.	0·8	37·5	10·5	46·7	5·3	11·1	7·2	4·7	2·5
2.	0·9	39·9	10·5	44·3	5·3	6·5	4·9	3·6	3·1
3.	1·0	42·1	10·5	42·1	5·3	6·0	4·0	2·8	2·4
4.	1·1	44·0	10·5	40·2	5·3	5·0	3·3	1·7	1·2
5.	1·2	46·0	10·5	38·2	5·3	5·5	3·5	1·6	0·4
6.	1·3	47·6	10·5	36·6	5·3	8·5	4·5	2·0	0·8
7.	1·4	49·1	10·5	35·1	5·3	21·5	5·9	3·5	1·8
8.	1·5	50·5	10·5	33·7	5·3	45·0	7·5	4·5	3·0

Table 4.

The above results are plotted as isothermal curves of viscosity against composition in Fig. 10.

These eight slags are distributed over four different quaternary phase volumes. This is illustrated in Fig. 12, which shows the requisite section through McCaffery's[40] version of the lime-alumina-silica-magnesia phase model. The position of the slag series examined is indicated by the dotted line. The positions of the five ternary planes which constitute the boundaries of the four quaternaries crossed, are indicated on the viscosity curves (Fig. 10), by arrows lettered a, b, c and d.

The planes akermanite-calcium-sesquisilicate-gehlenite and akermanite-calcium orthosilicate-gehlenite have no corresponding breaks in the viscosity curves which would

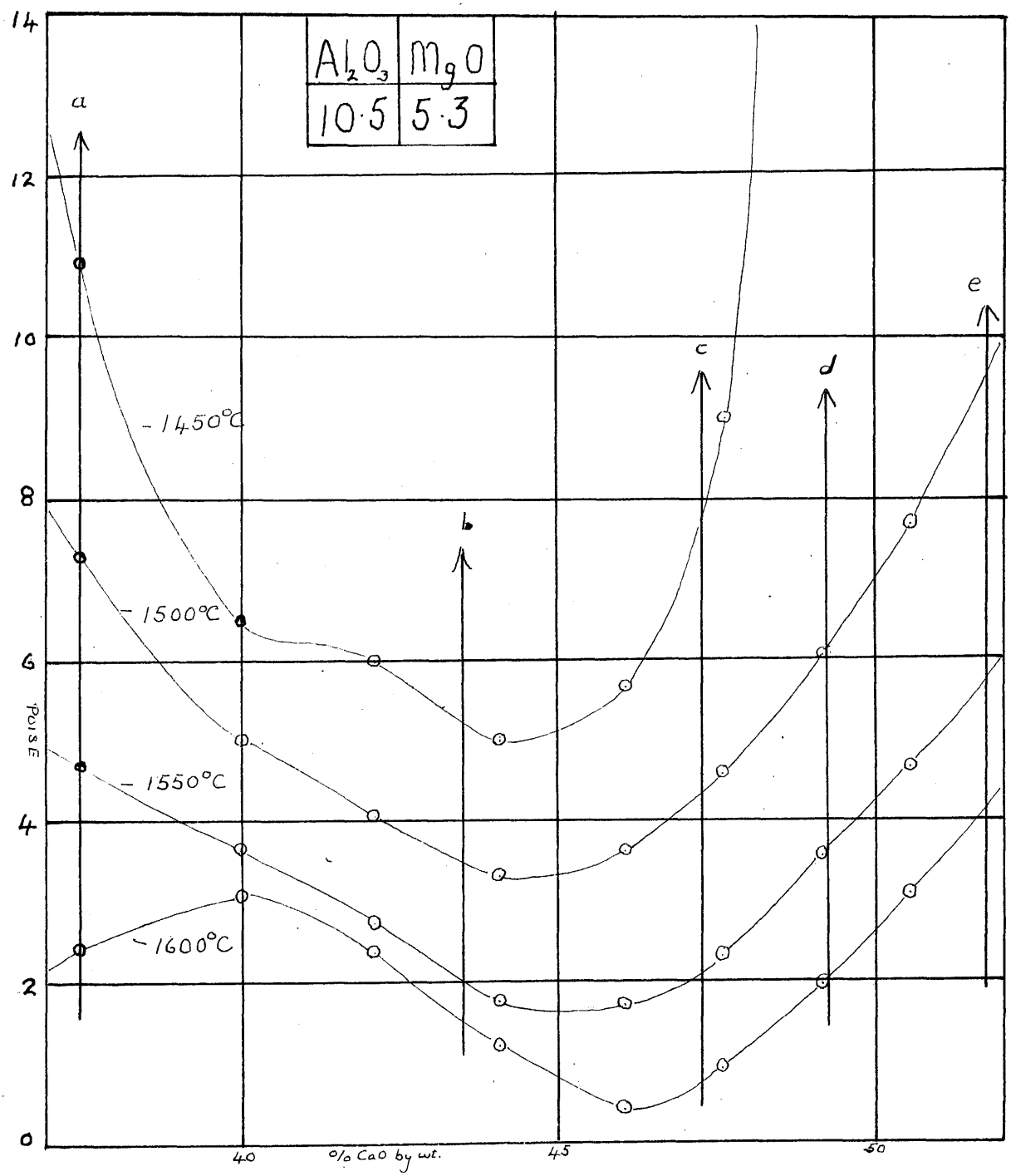

Al_2O_3 | MgO
10·5 | 5·3
a
b
c
d
e
1450°C
1500°C
1550°C
1600°C
POISE
0
2
4
6
8
10
12
14
40
45
50
% CaO by wt.

Figure 10

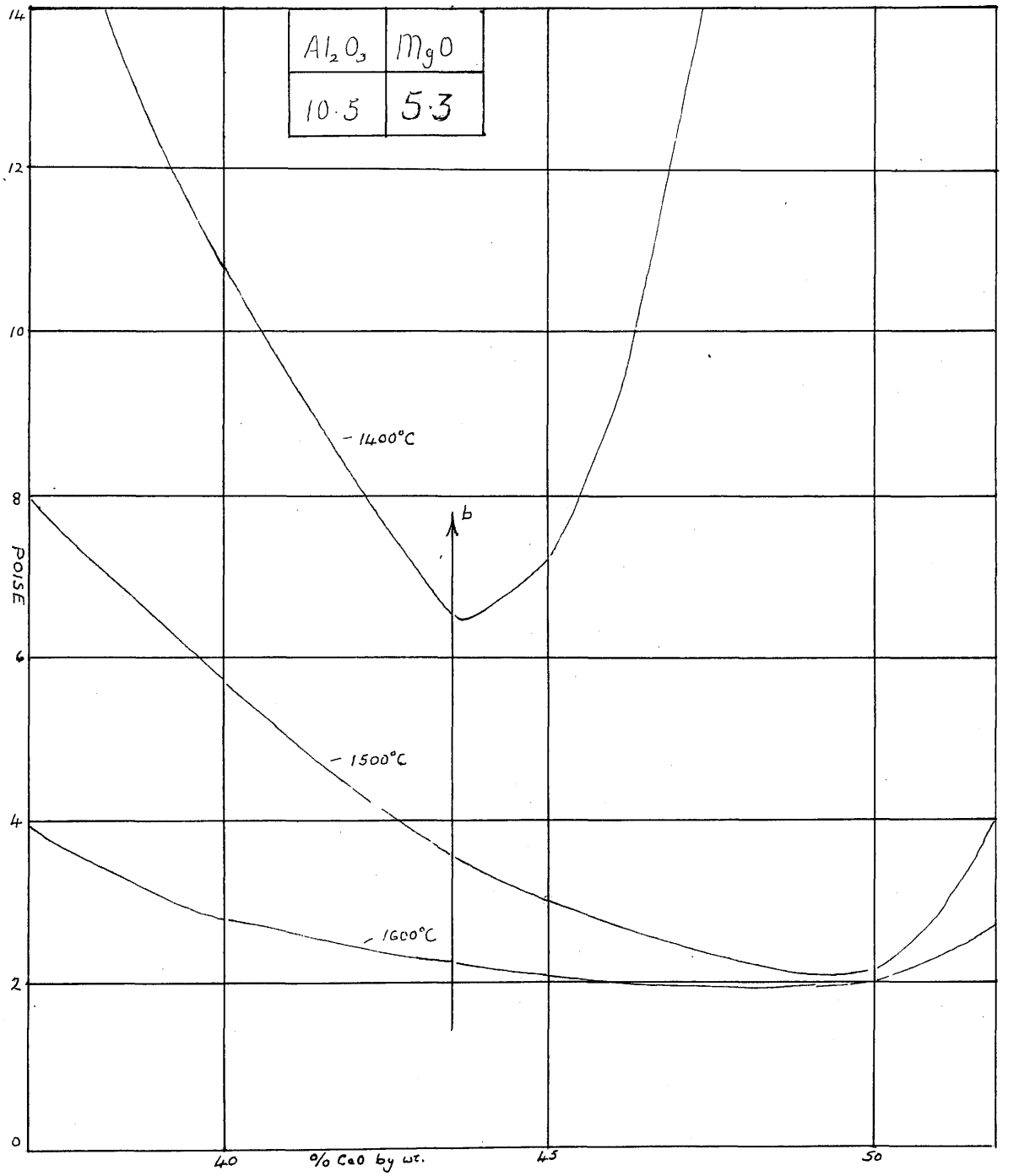
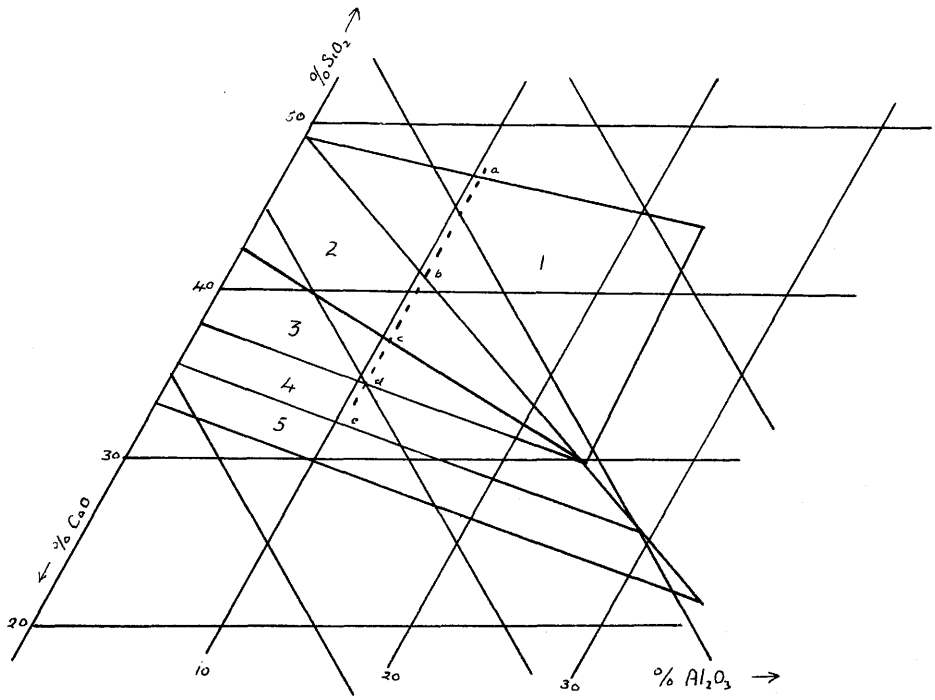

Al_2O_3 | MgO
10·5 | 5·3
1400°C
1500°C
1600°C
b
POISE
14
12
10
8
6
4
2
0
40
45
50
% CaO by wt.

Figure 11



Section at 5·3% MgO

Phase Volumes.

1. Akermanite-Anorthite-Calcium metasilicate-Gehlenite.
2. Akermanite-Calcium sesquisilicate-Calcium metasilicate-Gehlenite.
3. Akermanite-Calcium sesquisilicate-Calcium orthosilicate-Gehlenite.
4. Akermanite-Monticellite-Calcium orthosilicate-Gehlenite.
5. Magnesia-Monticellite-Calcium orthosilicate-Gehlenite.

Figure 12.

which would/ suggest that the phase changes involved in crossing these planes cause any irregular effect on the viscosity. Of a and e is the ternary planes, akermanite-anorthite-calcium metasilicate and ~~monticellite~~-monticellite-calcium orthosilicate-gehlenite, no definite statements can be made. They are too near the fringes of the range examined.

The remaining phase boundary b, the ternary akermanite - gehlenite-calcium metasilicate is clearly refelcted in the viscosity curves by a minimum. The phase boundary occurs at 43·6% lime while the minimum occurs at 44·0% lime in the 1450°C curve. As the temperature rises the minimum moves towards a higher lime content; thus at 1600°C the minimum occurs at 46% lime. It is suggested that this shift is due to the effect of temperature increasing the degree of dissociation of the ternary constituents.

It is interesting to note that the ternary which corresponds to the minimum, namely the akermanite-gehlenite-calcium metasilicate system, includes the binary calcium metasilicate-gehlenite which it was suggested caused the minimum in the isothermal curves of the ternary slags examined. It will also be recalled that Rait, McMillan and Hay[27] and Herty[26] have both found a minimum in the lime-silica viscosity isothermals corresponding to the compound calcium metasilicate.

The next section includes further evidence of the existence of calcium metasilicate, akermanite and gehlenite in the liquid state. There is therefore considerable reason to believe that these minerals are not wholly dissociated in the liquid state, and that consequently the physical properties of liquid slags are a function of their mineral constitution. In Fig. 11. McCaffery's[31] results for the same melts are illustrated. There is very little agreement between the two sets of results. In view, however, of the serious fault existing in McCaffery's apparatus, (see Chapt.2) this is not surprising. It is worth noting, however, that the minimum in McCaffery's isothermal curve for 1400°C, closely corresponds to the akermanite-calcium metasilicate-gehlenite ternary plane, and that in the 1500 and 1600°C curves the minimum has shifted towards a composition of higher lime content.

The effect of the addition of 5·3% magnesia on the viscosity of these six lime-alumina-silica slags, between 1450 and 1600°C is illustrated in Figs 13 - 15. In every case the magnesia reduced the viscosity, the effect being greatest with the slags of higher lime content. This is in general agreement with McCaffery[31], who found that magnesia consistently decreased the viscosity of synthetic blast furnace slags.

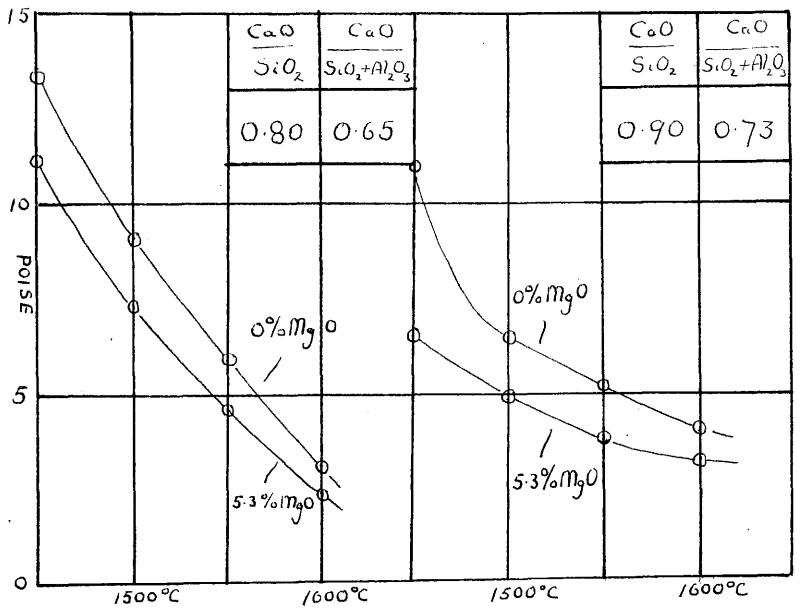


Figure 13

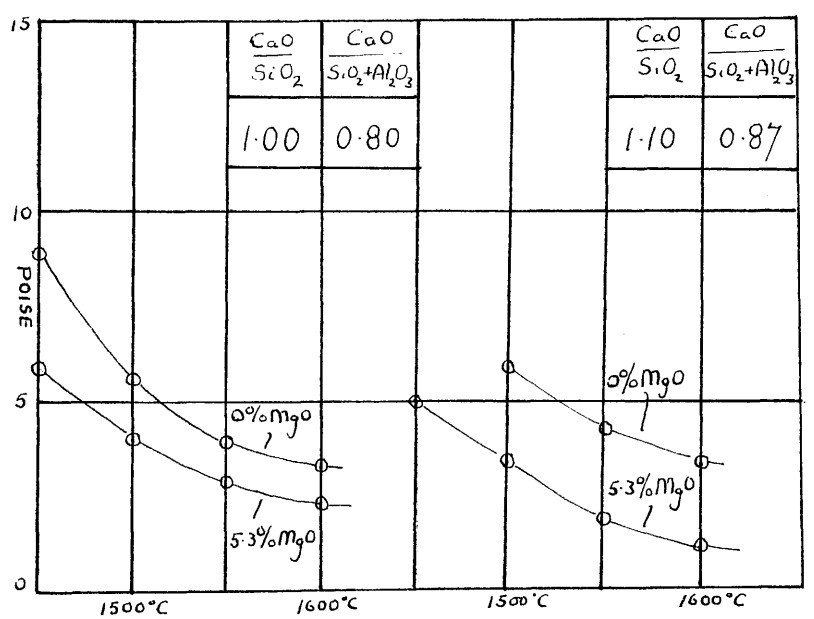


Figure 14

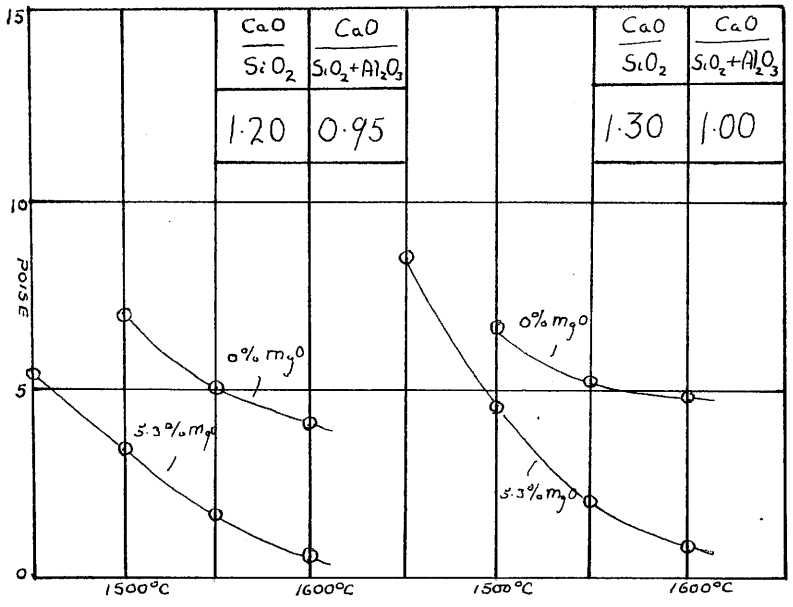

15
10
5
0
POISE
CaO / SiO2
CaO / SiO2+Al2O3
1·20
0·95
1·30
1·00
0% MgO
5·3% MgO
0% MgO
5·3% MgO
1500°C
1600°C
1500°C
1600°C

Figure 15

This effect of magnesia would suggest that dolomite additions would have beneficial results on the running of a blast furnace.

(3) Lime-Alumina-Silica-Magnesia-Titania Slags.

An addition of 5% titania was made to each of the eight quaternary slags described above. The compositions of the resultant quinternary slags are given in Table 5, together with the viscosity coefficient for 50 degree intervals from 1300 - 1600°C.

These figures are plotted as isothermal curves of viscosity against composition in Fig. 20. The significance of these curves with respect to constituent constitution will be considered in the next section.

Viscosity-temperature curves of lime-alumina-silica, lime-alumina-silica-magnesia, and lime-alumina-silica-magnesia-titania are compared in Figs. 16 to 19. The ternary, quaternary, and quinternary curves compared in each diagram, are those of slags of the same CaO/SiO_2 and $CaO/SiO_2 + Al_2O_3$ ratio.

The titania addition increased the viscosity of the quaternary slags of CaO/SiO_2 0·8 - 1·1 over the temperature range examined. In the case of the slag of CaO/SiO_2 ratio 0·8, the viscosity was increased to such an extent that the viscosity-temperature curve lies wholly above that of the parent ternary slag. With the slags of CaO/SiO_2 ratio 0·9 - 1·1, the titania only partially counteracted

KEY TO FIGS. 16 - 19.

———— Lime-Alumina-Silica.

--------- Lime-Alumina-Silica-Magnesia.

—o o o— Lime-Alumina-Silica-Magnesia-Titania.

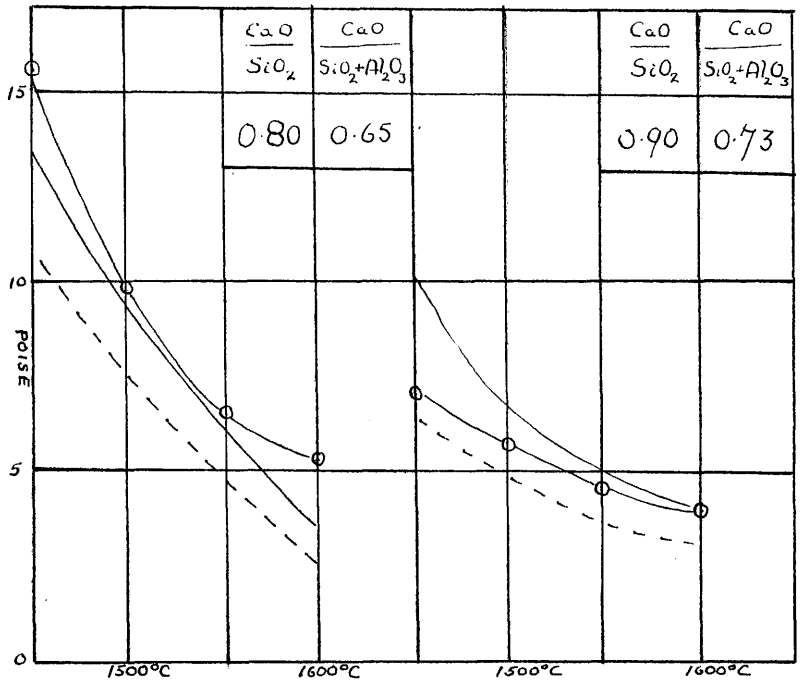


Figure 16

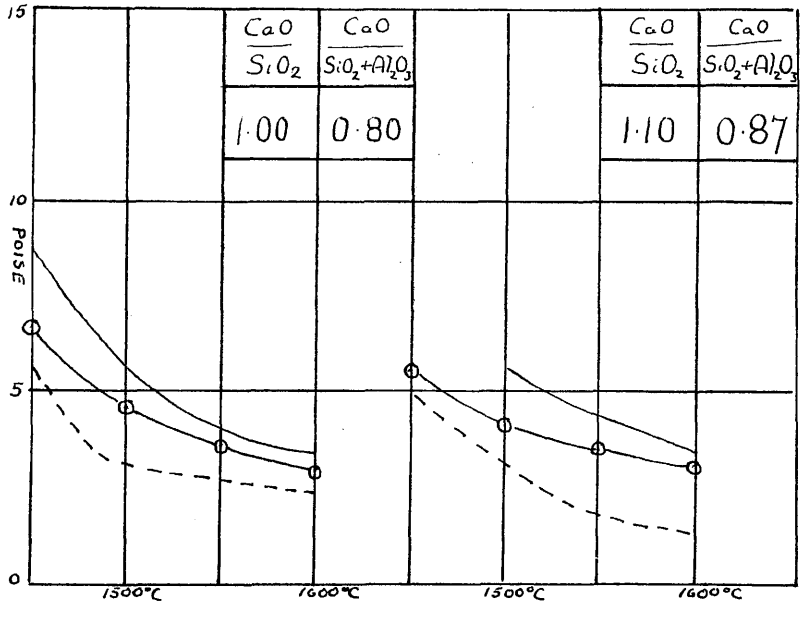


Figure 17

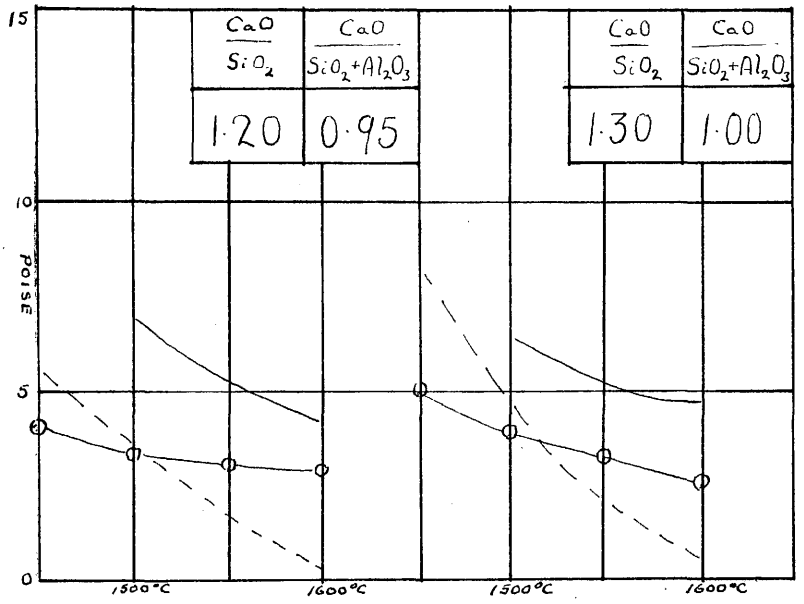


Figure 18

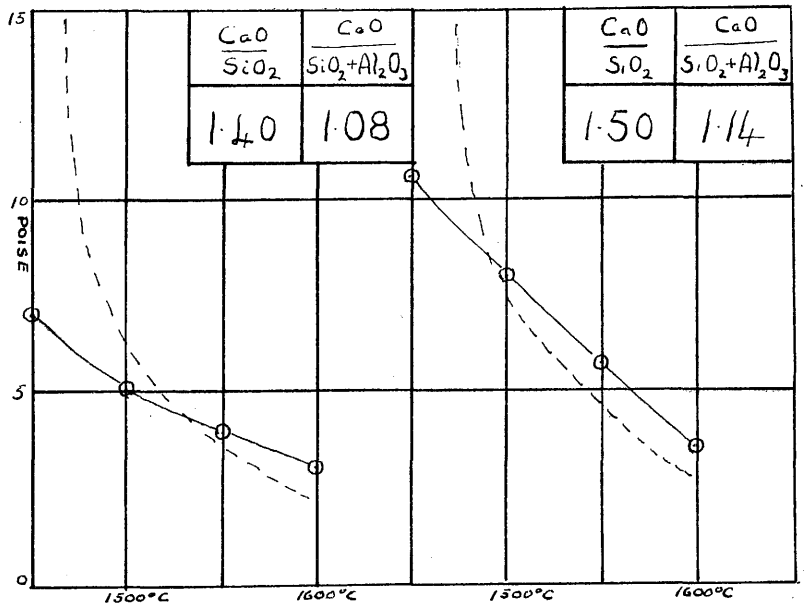


Figure 19

No.	CaO/SiO_2	Composition -- Wt.%.					Viscosity in poise at :-						
		CaO	SiO_2	Al_2O_3	MgO	TiO_2	1300°C	1350°C	1400°C	1450°C	1500°C	1550°C	1600°C
1.	0.8	35.6	44.4	10.0	5.0	5.0	--	--	--	15.5	9.7	6.5	5.2
2.	0.9	37.9	42.1	10.0	5.0	5.0	--	19.2	8.3	7.1	5.8	4.6	4.0
3.	1.0	40.0	40.0	10.0	5.0	5.0	21.9	15.0	9.7	6.7	4.7	3.6	3.0
4.	1.1	41.9	38.1	10.0	5.0	5.0	--	--	--	5.6	4.2	3.5	3.0
5.	1.2	43.5	36.5	10.0	5.0	5.0	--	7.1	5.5	4.2	3.3	3.0	2.8
6.	1.3	45.2	34.8	10.0	5.0	5.0	--	--	--	5.0	3.8	3.2	2.6
7.	1.4	46.7	33.3	10.0	5.0	5.0	--	--	--	7.0	5.0	4.0	3.0
8.	1.5	48.0	32.0	10.0	5.0	5.0	--	--	--	10.6	8.0	5.7	3.5

Table 5.

counteracted/ the effect the magnesia had on the viscosity of the ternary slag.

For the slags of higher basicity, CaO/SiO_2 1·2 - 1·5, the titania addition had the effect of increasing the viscosity of the quaternary slag at temperatures above 1500°C; but decreased it below this temperature. This effect is probably due to the titania lowering the fusion point of the slag.

The quinternary slags of CaO/SiO_2 1·2 - 1·5 are considerably more fluid than the corresponding ternary slags, over the range 1450 - 1600°C. The ternary slags of CaO/SiO_2 ratio 1·4 and 1·5 corresponding to the quaternary and quinternary slags of Fig. 19 are below the liquidus temperature over the temperature range employed.

The effect of titania is to increase the viscosity of the quaternary slags, and thus offset the effect the magnesia had on the ternary slags. This effect is greatest in the less basic slags. Titania also has the effect of lowering the fusion point and as a result some of the quinternary slags are quite fluid at temperatures at which the quaternary and ternary slags are viscous or even solid.

(4) <u>The effect of varying the alumina content of lime-alumina-silica-magnesia-titania slags.</u>

Altogether 56 lime-alumina-silica-magnesia-titania

Table 6.

No.	CaO/SiO_2	Composition -- wt.%.					Viscosity in poises at :-						
		CaO	SiO_2	Al_2O_3	MgO	TiO_2	1300°C	1350°C	1400°C	1450°C	1500°	1550°C	1600°C
1	0.8	35.6	44.4	10.0	5.0	5.0	--	--	--	15.5	9.7	6.5	5.2
2	0.8	34.6	43.1	12.5	4.9	4.9	--	--	--	18.1	11.3	7.1	5.9
3	0.8	33.6	42.0	15.0	4.7	4.7	--	--	--	21.2	12.8	7.9	6.8
4	0.8	32.7	40.8	17.5	4.5	4.5	--	--	--	26.0	12.9	9.1	8.2
5	0.8	31.7	39.5	20.0	4.4	4.4	--	--	--	31.6	18.1	12.2	11.0
6	0.8	30.7	38.3	22.5	4.3	4.3	--	--	--	38.0	25.0	19.0	14.5
7	0.8	29.6	37.1	25.0	4.1	4.1	--	--	--	--	--	30.0	21.0
8.	0.9	37.9	42.1	10.0	5.0	5.0	--	19.2	8.3	7.1	5.8	4.6	4.0
9	0.9	36.8	40.9	12.5	4.9	4.9	--	22.1	14.1	9.8	6.9	6.3	5.8
10	0.9	35.8	39.8	15.0	4.7	4.7	--	25.2	19.3	12.2	7.9	7.4	7.0
11	0.9	34.8	38.6	17.5	4.5	4.5	--	28.9	24.1	13.0	8.4	7.0	6.2
12	0.9	33.7	37.4	20.0	4.4	4.4	--	33.2	24.0	13.2	9.1	7.1	6.0
13	0.9	32.7	36.3	22.5	4.3	4.3	--	40.0	22.0	15.5	10.0	7.9	6.8
14	0.9	31.6	35.1	25.0	4.1	4.1	--	--	40	22.0	13.3	9.7	8.3
15	1.0	40.0	40.0	10.0	5.0	5.0	21.9	15.0	9.7	6.7	4.7	3.6	3.0

Table 6. Contd.

No.	CaO/SiO_2	Composition -- wt.%.					Viscosity in poises at : --						
		CaO	SiO_2	Al_2O_3	MgO	TiO_2	1300°C	1350°C	1400°C	1450°C	1500°C	1550°C	1600°C
16	1.0	38.8	38.8	12.5	4.9	4.9	23.8	18.1	13.0	9.5	7.8	7.1	6.6
17	1.0	37.8	37.8	15.0	4.7	4.7	--	21.7	15.8	12.2	10.0	9.2	8.8
18	1.0	36.7	36.7	17.5	4.5	4.5	--	--	--	14.9	10.5	9.2	8.3
19	1.0	35.6	35.6	20.0	4.4	4.4	--	--	--	16.5	10.9	8.8	7.0
20	1.0	34.4	34.4	22.5	4.3	4.3	--	--	--	18.5	11.5	8.9	7.1
21	1.0	33.4	33.4	25.0	4.1	4.1	--	--	--	23.0	13.3	10.0	8.1
22	1.1	41.9	38.1	10.0	5.0	5.0	--	--	--	5.6	4.2	3.5	3.0
23	1.1	40.7	37.0	12.5	4.9	4.9	--	--	--	8.1	6.1	5.5	5.0
24	1.1	39.6	36.0	15.0	4.7	4.7	--	--	--	10.3	7.1	6.6	6.2
25	1.1	38.4	35.0	17.5	4.5	4.5	--	--	--	12.1	7.4	6.8,	6.0
26	1.1	37.2	33.8	20.0	4.4	4.4	--	--	--	13.5	7.8	6.5	5.6
27	1.1	36.1	32.8	22.5	4.3	4.3	--	--	--	15.5	8.3	6.5	5.7
28	1.1	34.9	31.8	25.0	4.1	4.1	--	--	--	18.4	9.6	7.2	6.0
29.	1.2	43.5	36.5	10.0	5.0	5.0	--	7.1	5.5	4.2	3.3	3.0	2.8
30	1.2	42.2	35.5	12.5	4.9	4.9	--	--	--	5.8	3.5	3.0	2.8
31	1.2	41.1	34.5	15.0	4.7	4.7	--	--	--	7.0	3.6	3.0	2.9

Table 6. Contd.

No.	CaO/SiO_2	Composition -- wt.%.					Viscosity in poises at : --						
		CaO	SiO_2	Al_2O_3	MgO	TiO_2	1300°C	1350°C	1400°C	1450°C	1500°C	1550°C	1600°C
32	1.2	39.9	33.5	17.5	4.5	4.5	--	--	--	8.2	3.6	3.1	3.0
33	1.2	38.6	32.4	20.0	4.4	4.4	--	--	--	9.2	3.9	3.3	3.1
34	1.2	37.5	31.4	22.5	4.3	4.3	--	--	--	9.9	4.2	3.5	3.4
35	1.2	36.2	30.4	25.0	4.1	4.1	--	--	--	10.0	4.8	3.7	3.5
36	1.3	45.2	34.8	10.0	5.0	5.0	--	--	--	5.0	3.8	3.2	2.6
37	1.3	43.9	33.8	12.5	4.9	4.9	--	--	--	5.0	3.4	3.0	2.7
38	1.3	42.7	32.9	15.0	4.7	4.7	--	--	--	5.2	3.0	2.7	2.5
39	1.3	41.5	31.9	17.5	4.5	4.5	--	--	--	6.0	3.3	2.9	2.6
40	1.3	40.2	30.9	20.0	4.4	4.4	--	--	--	7.5	3.7	3.0	2.8
41	1.3	38.9	30.0	22.5	4.3	4.3	--	--	--	9.0	4.0	3.0	2.5
42	1.3	37.7	29.0	25.0	4.1	4.1	--	--	--	10.0	4.0	3.2	2.5
43	1.4	46.7	33.3	10.0	5.0	5.0	--	--	--	7.0	5.0	4.0	3.0
44	1.4	45.3	32.4	12.5	4.9	4.9	--	--	--	4.8	3.2	2.6	2.3
45	1.4	44.1	31.5	15.0	4.7	4.7	--	--	--	4.0	2.8	2.4	2.3
46	1.4	42.8	30.6	17.5	4.5	4.5	--	--	--	4.4	3.2	2.8	2.5
47	1.4	41.5	29.6	20.0	4.4	4.4	--	--	--	6.7	3.8	3.0	2.3

Table 6. Contd.

No.	CaO/SiO_2	Composition -- wt.%.					Viscosity in poises at : --						
		CaO	SiO_2	Al_2O_3	MgO	TiO_2	1300°C	1350°C	1400°C	1450°C	1500°C	1550°C	1600°C
48	1.4	40.2	28.7	22.5	4.3	4.3	--	--	--	9.5	4.0	3.0	2.4
49	1.4	38.9	27.8	25.0	4.1	4.1	--	--	--	12.5	4.5	3.4	2.8
50	1.5	48.0	32.0	10.0	5.0	5.0	--	--	--	10.6	8.0	5.7	3.5
51	1.5	46.7	31.0	12.5	4.9	4.9	--	--	--	6.5	4.8	3.8	3.1
52	1.5	45.4	30.2	15.0	4.7	4.7	--	--	4.7	3.1	3.1	3.0	3.0
53	1.5	44.1	29.3	17.5	4.5	4.5	--	--	--	3.4	3.3	3.2	3.1
54	1.5	42.7	28.4	20.0	4.4	4.4	--	--	--	5.6	3.8	3.5	3.3
55	1.5	41.3	27.6	22.5	4.3	4.3	--	--	--	9.8	4.5	3.8	3.3
56	1.5	40.0	26.7	25.0	4.1	4.1	--	--	--	17.0	5.5	4.3	3.5

titania/ slags have been examined. The compositions of these together with their viscosity coefficient at 50 degree intervals are given in Table 6. These results have been plotted in the form of isothermal curves of viscosity against composition in Figs. 20 - 26. Clearly no general statements can be made regarding the effect on the viscosity of varying the CaO/SiO_2 ratio. In some cases an increase of lime increases, and in others decreases the viscosity.

In Figs. 27 - 30, the results are plotted in the form of isovis curves on triangular axes of lime, alumina and silica. These figures can be regarded as "double sections" through the quinternary isovis plot at 5% magnesia and 5% titania. These diagrams entail a slight approximation since both the magnesia and titania contents of some of the slags fall as low as 4·1%. However, it was thought worth while including these diagrams in view of their clearer pictorial representation of the effect on the viscosity of varying the lime, alumina, or silica content.

A point brought out by these diagrams is the persistent effect of alumina to increase viscosity. These are, however, exceptions to this, for example a slag of CaO/SiO_2 0·9; Al_2O_3 15%; MgO 4·7% and TiO_2 4·7%, has a viscosity of 7 poise at 1600°C; but if the Al_2O_3

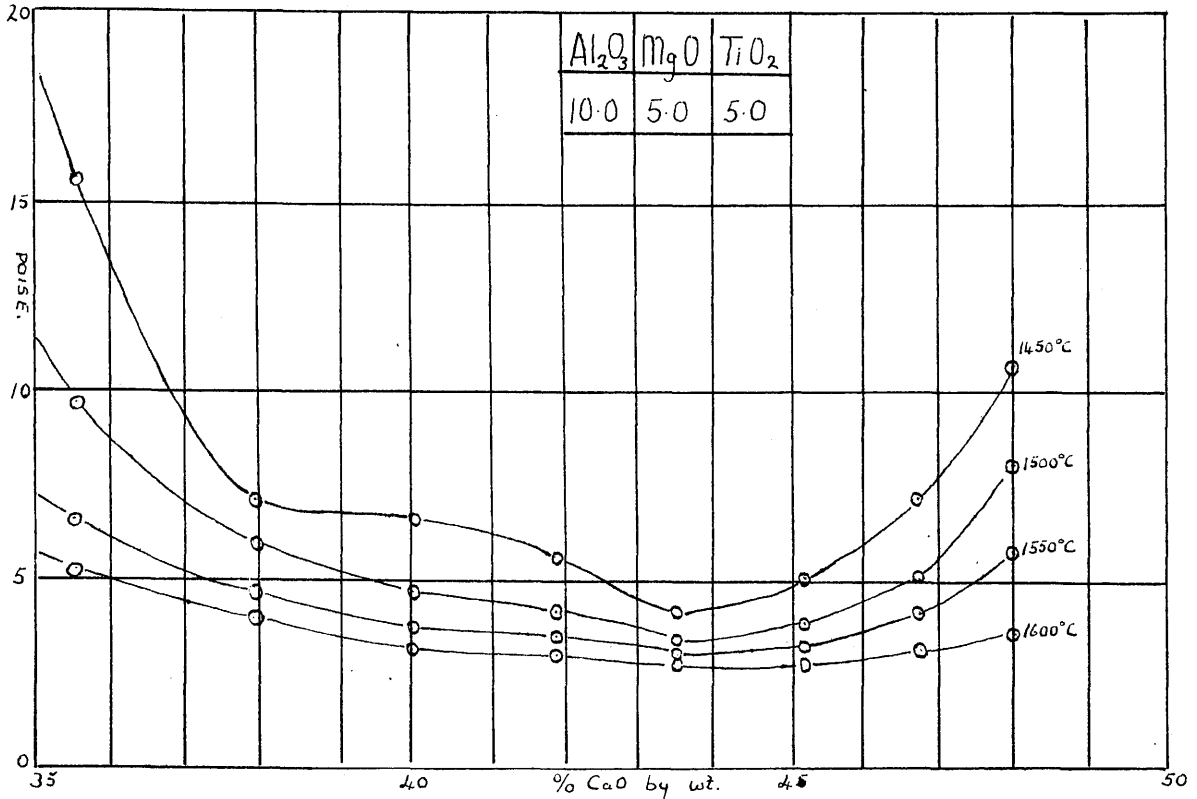


Figure 20

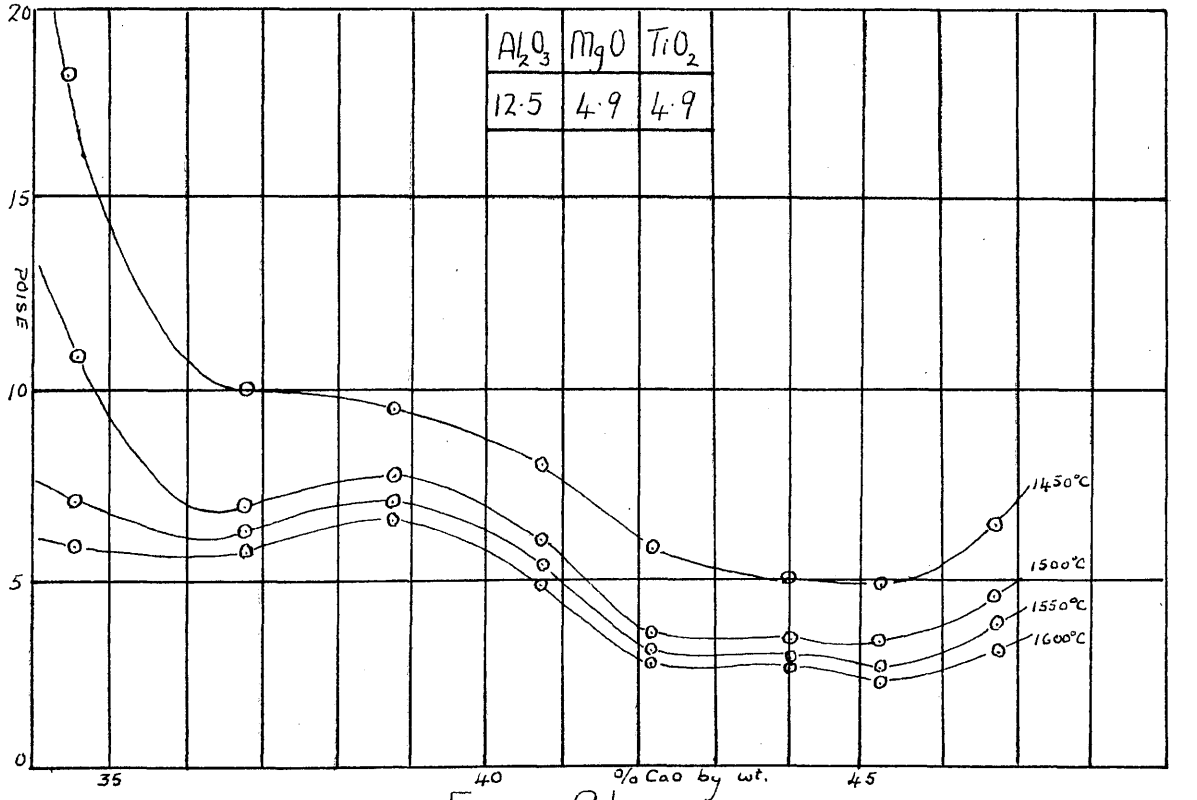


Figure 21

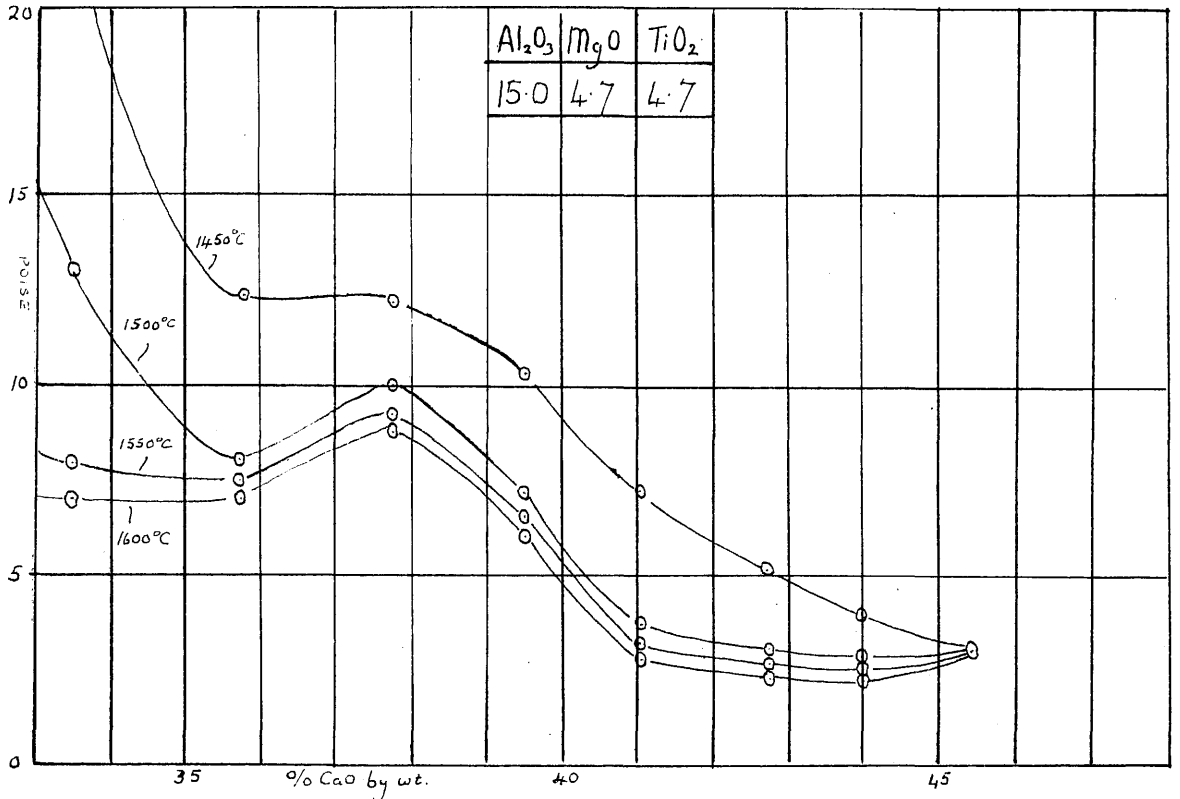


Figure 22

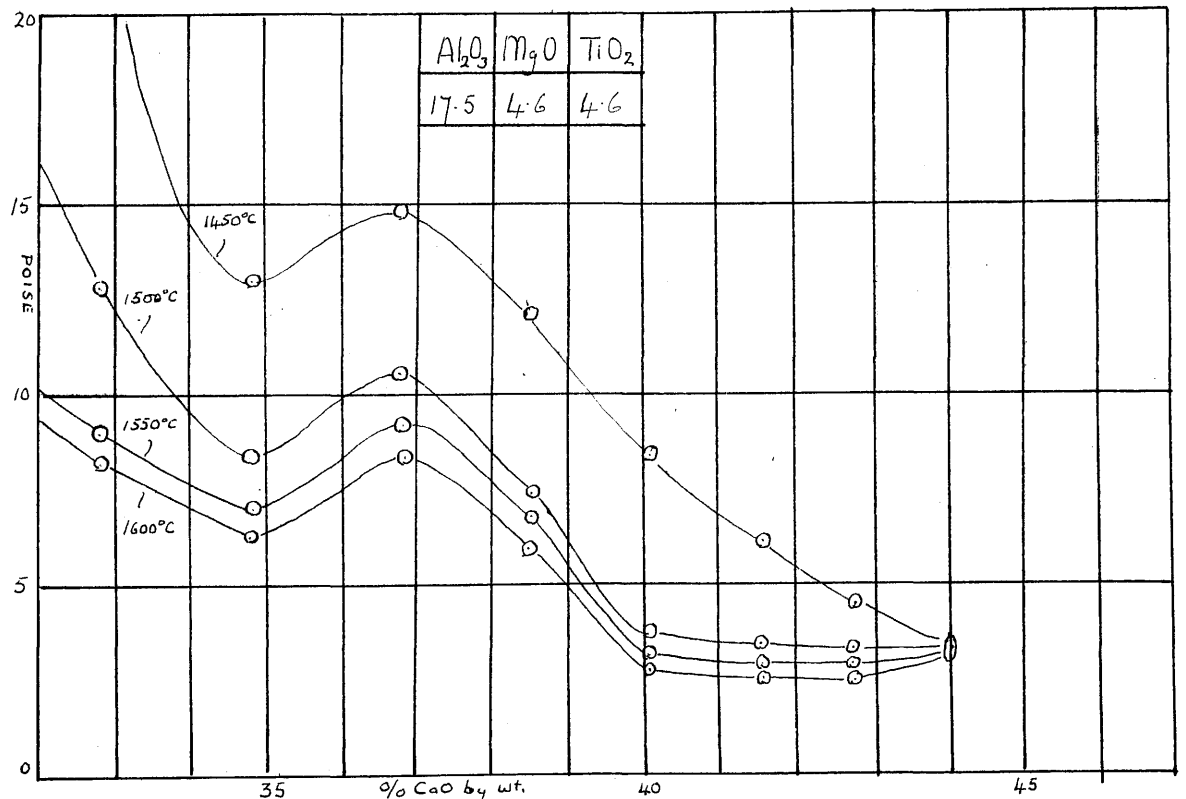


Figure 23

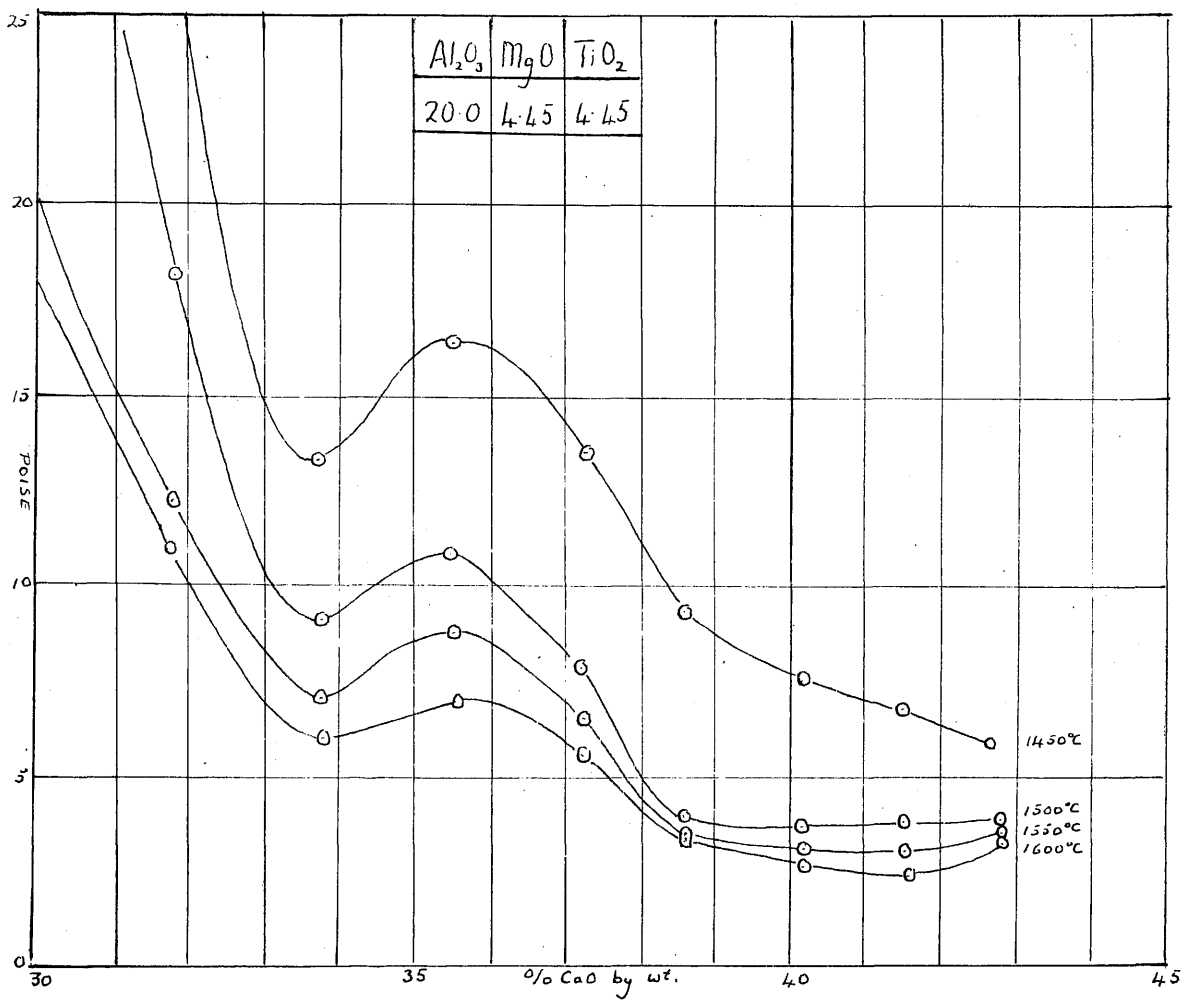

Al_2O_3 | MgO | TiO_2
20·0 | 4·45 | 4·45
25
20
15
10
5
0
POISE
30
35
% CaO by wt.
40
45
1450°C
1500°C
1550°C
1600°C

Figure 24.

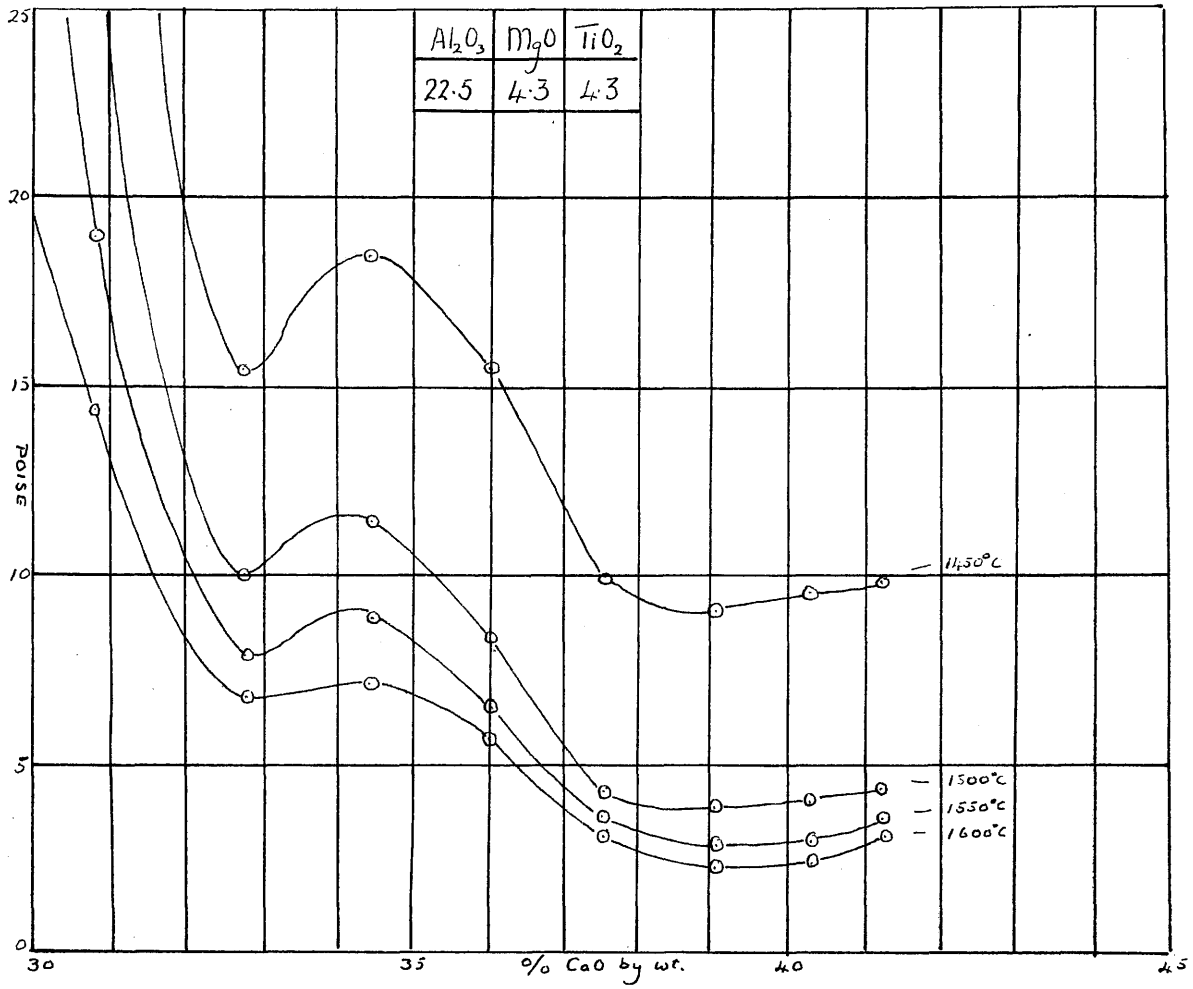

Al_2O_3 | MgO | TiO_2
22·5 | 4·3 | 4·3
25
20
15
10
5
0
POISE
30
35
40
45
% CaO by wt.
1450°C
1500°C
1550°C
1600°C

Figure 25

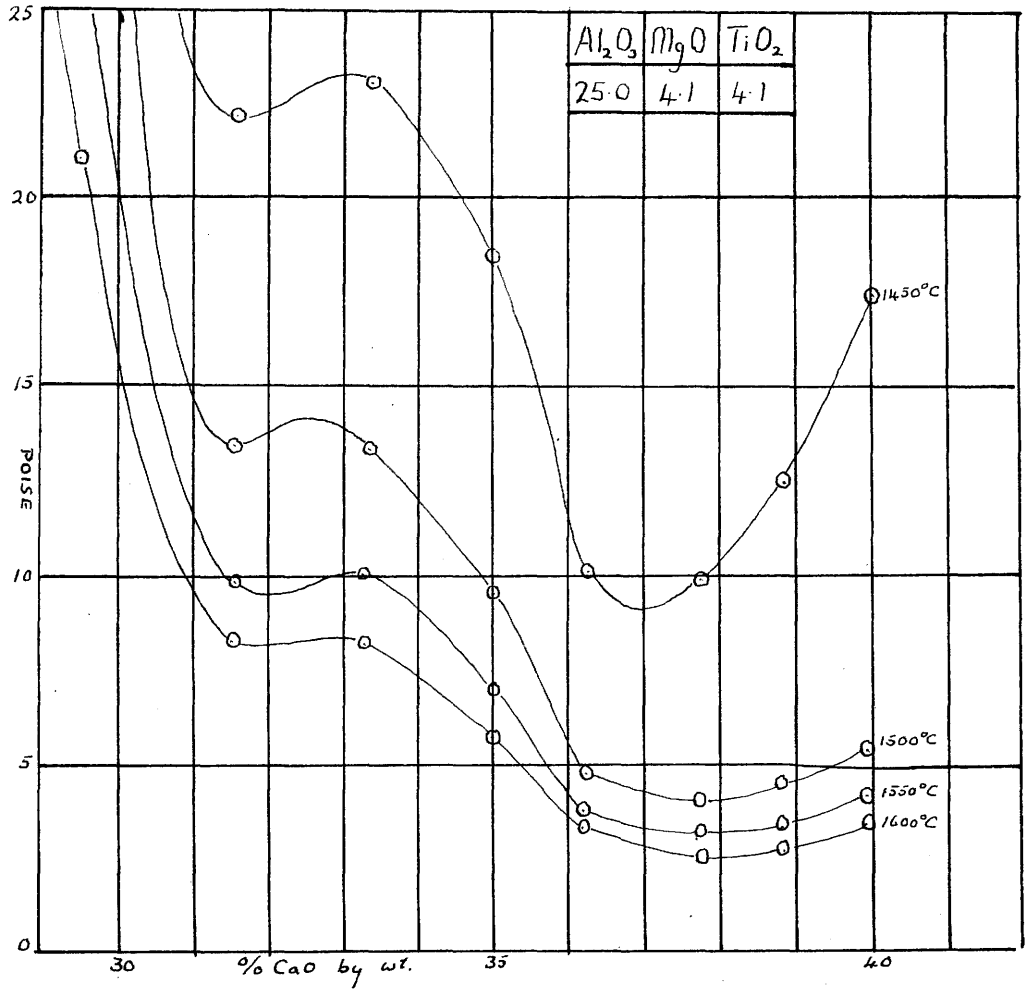

Al_2O_3 MgO TiO_2
25·0 4·1 4·1
25
20
15
10
5
0
POISE
30
% CaO by wt.
35
40
1450°C
1500°C
1550°C
1600°C

Figure 26

1450°C

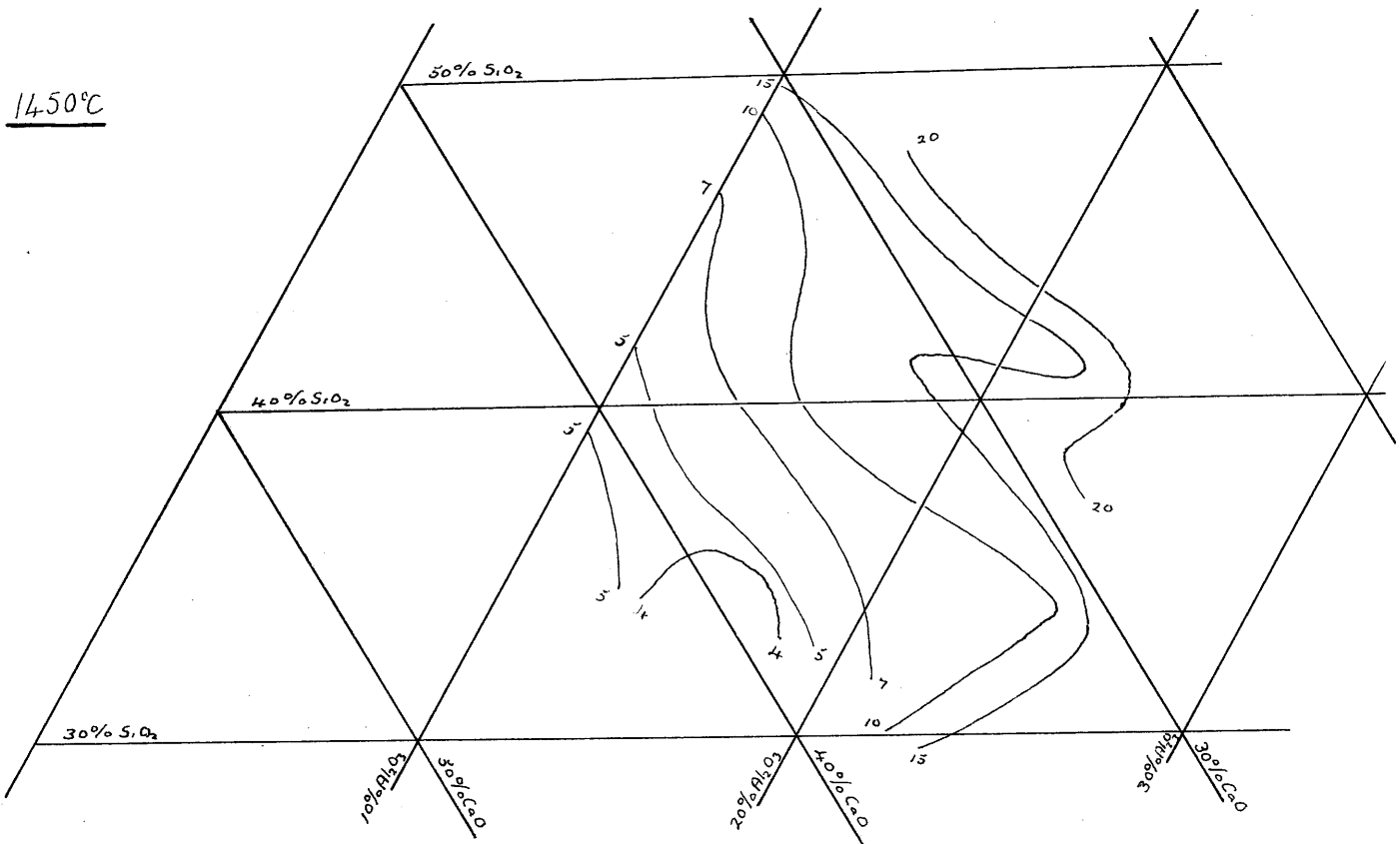


Figure 27

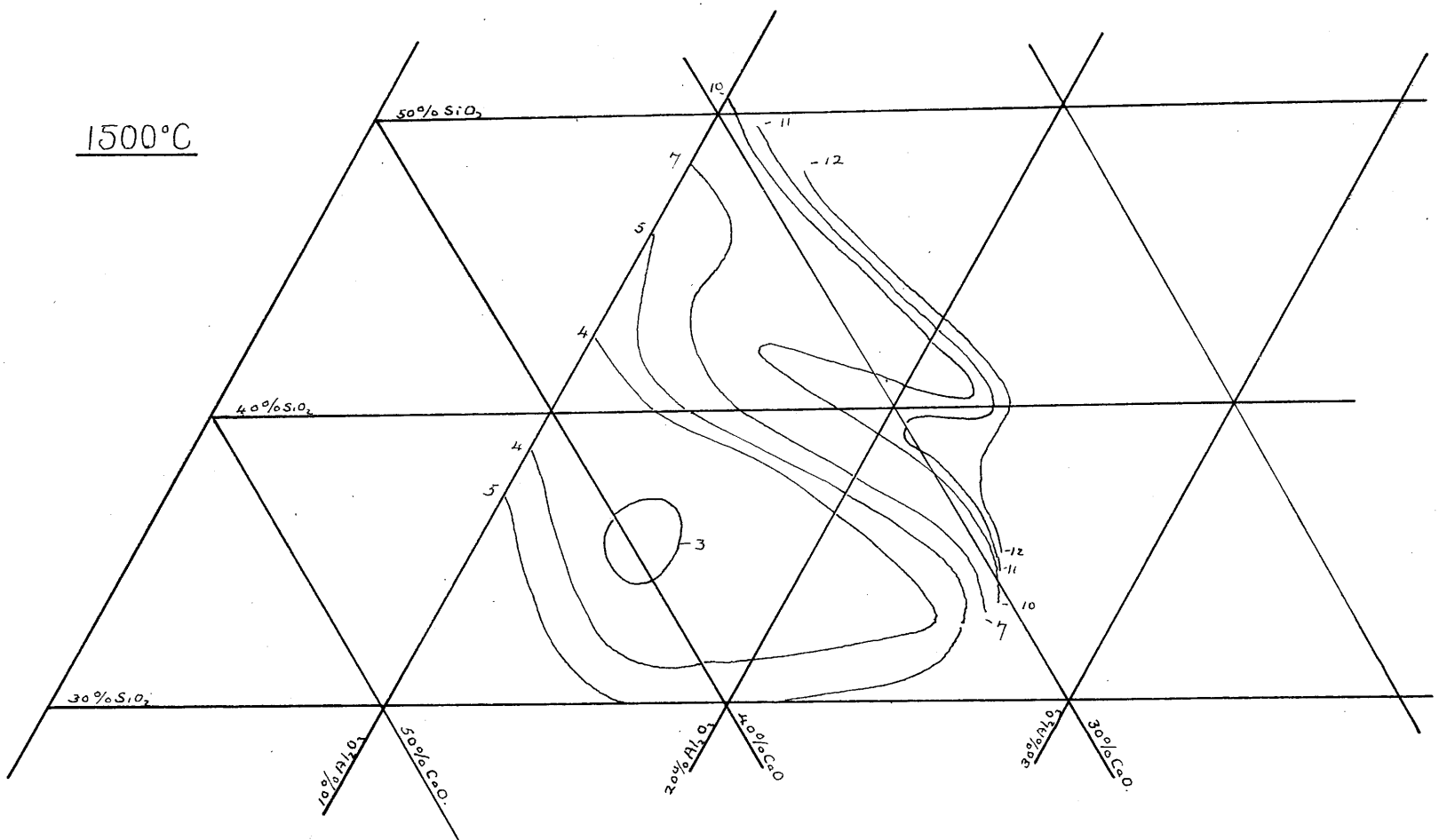

1500°C
50% SiO2
40% SiO2
30% SiO2
10% Al2O3
50% CaO
20% Al2O3
40% CaO
30% Al2O3
30% CaO
10
11
12
7
5
4
4
5
3
12
11
10
7

Figure 28

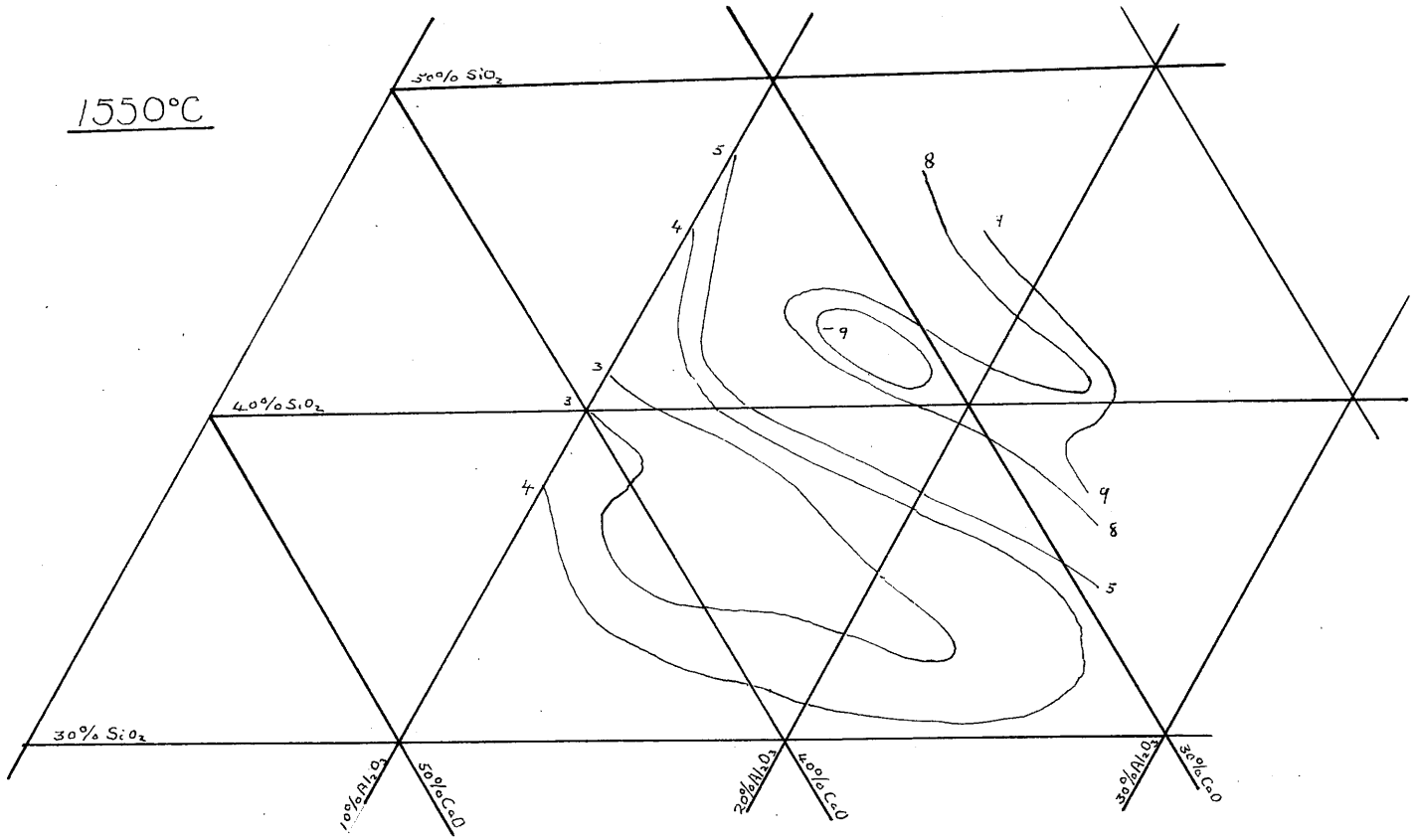

1550°C
50% SiO2
40% SiO2
30% SiO2
10% Al2O3
50% CaO
20% Al2O3
40% CaO
30% Al2O3
30% CaO
5
4
3
8
7
9
6
5
4
3

Figure 29

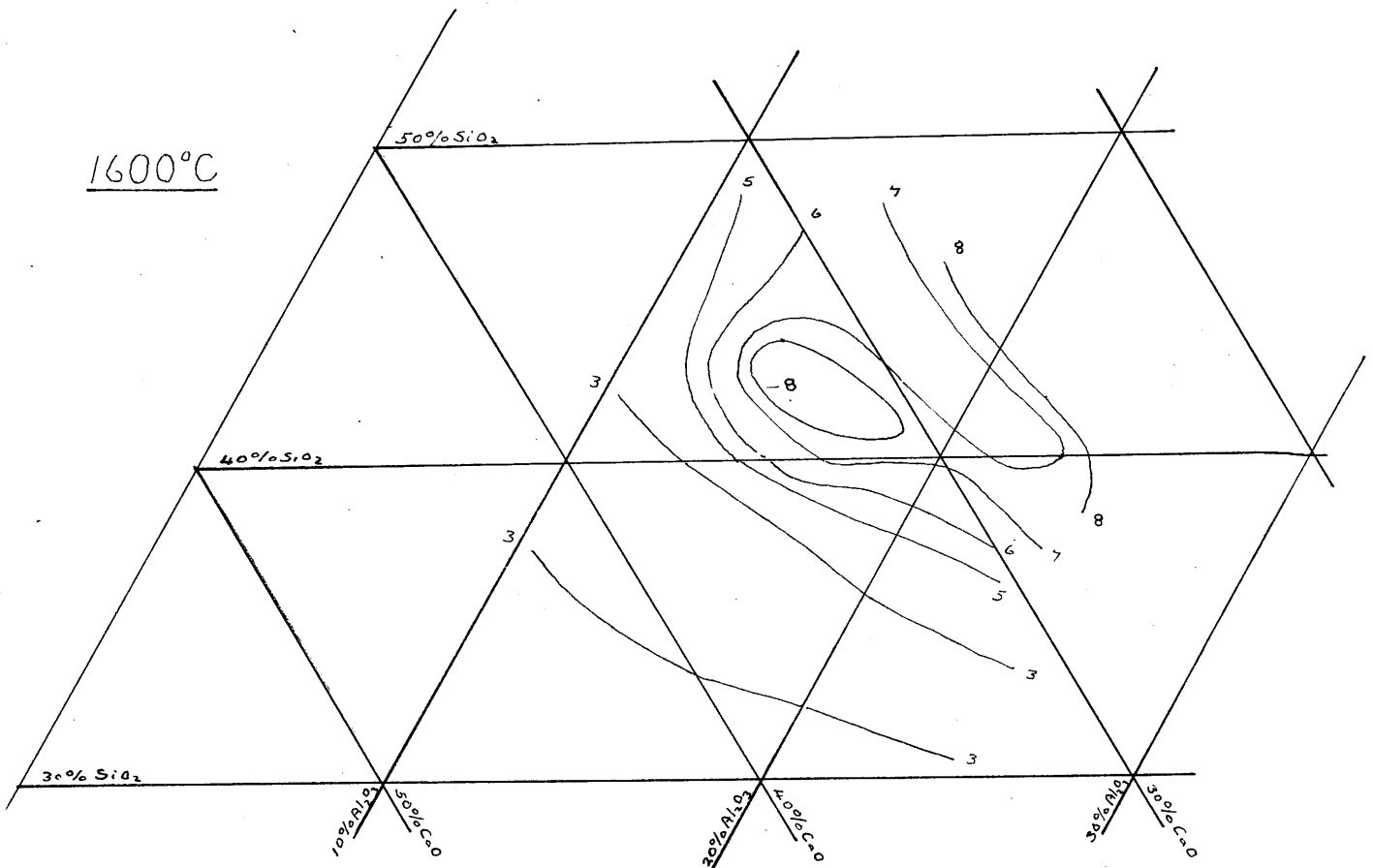

1600°C
50% SiO2
40% SiO2
30% SiO2
10% Al2O3
50% CaO
30% Al2O3
40% CaO
50% Al2O3
30% CaO
3
5
6
7
8

Figure 30

the Al_2O_3/ be increased to 20% the viscosity fall to 6 poise. (See slags 10 and 12 of Table 6).

It is clear from the viscosity-temperature curves considered above that none of the lime-alumina-silica-magnesia-titania slags are sufficiently viscous at working temperatures to cause difficulty in the running of a blast furnace. Indeed, owing to the titania lowering the fusion point, the results would suggest that a furnace smelting titaniferous ores might be successfully operated at lower temperatures than those normally employed. The explanation of difficulties experienced in handling slags containing no more than 5% titania, must therefore be sought elsewhere, since they apparently depend on the fulfilment of certain conditions which have not been realised in the present series of experiments.

The lime-alumina-silica-magnesia-titania phase diagram has not been worked out. It was therefore impossible to interpret the minima in the isothermal curves (Figs. 20 - 26) directly in the manner adopted for the quaternary and ternary slags. It was therefore decided to assume that the minima did correspond to ~~phase~~ constituent changes and attempt to deduce the constituents of the quaternary systems corresponding to the minima.

The compositions of the minima (which are given in Table 7), were plotted on a quinternary section in Fig. 31.

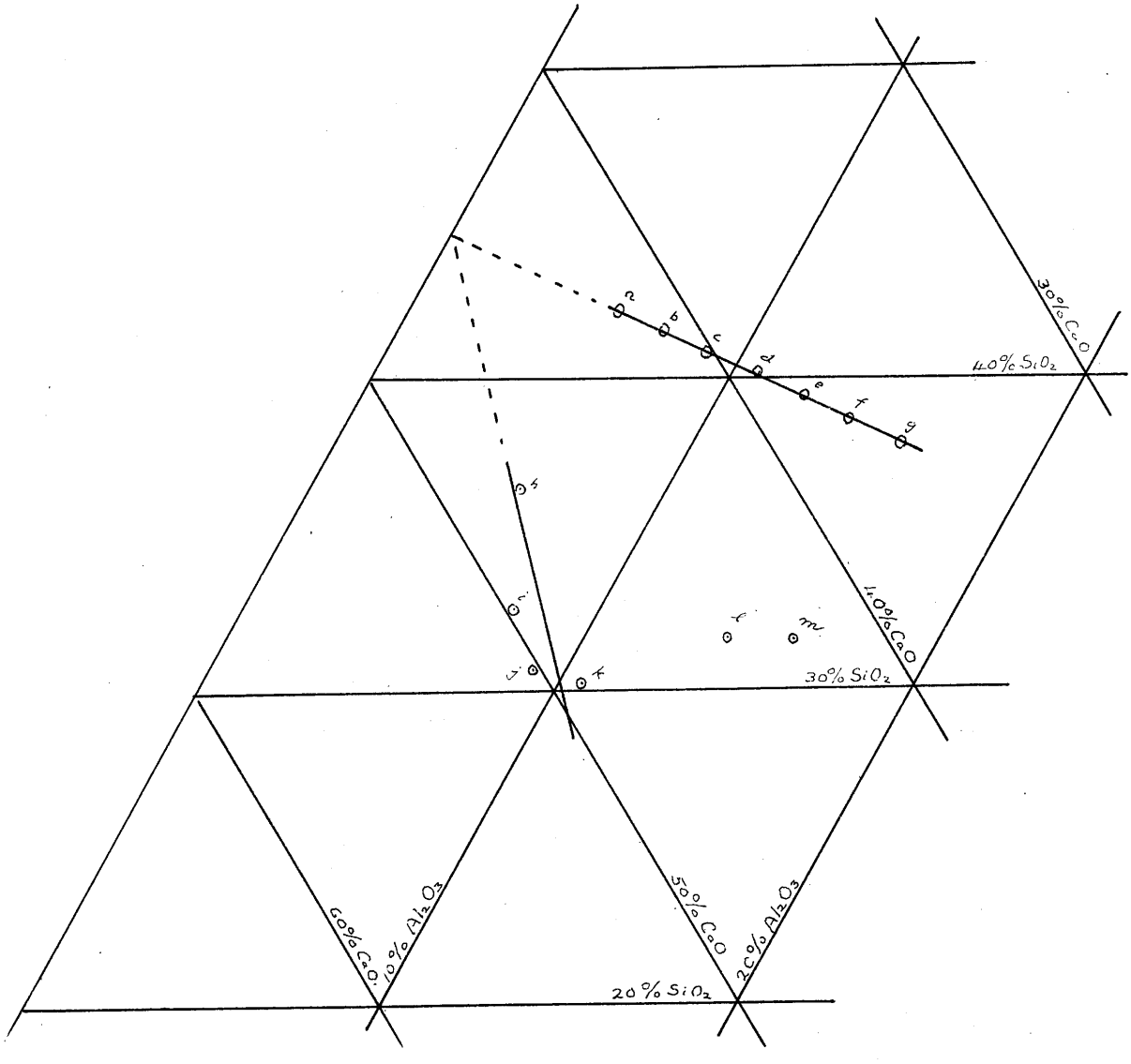

30% CaO
40% SiO2
40% CaO
30% SiO2
60% CaO, 10% Al2O3
50% CaO
20% Al2O3
20% SiO2
a
b
c
d
e
f
g
h
j
k
m
n
s

Figure 31

in Fig. 31./ Clearly they fall into two main groups, one of seven points, and the other of four points, each group forming a straight line. The two lines intersect on the line representing the double section, through the lime-magnesia-silica-titania quaternary. Two of the points (l and m) are not included by either of these straight lines.

The problem therefore resolved itself into fitting a quaternary system of constituents to each of these two lines. If the assumption is made that there is no intermediate constituent change, then three of the constituents should be common to each quaternary.

No.	Composition - wt %					Composition - moles.%				
	Al_2O_3	MgO	TiO_2	CaO	SiO_2	Al_2O_3	MgO	TiO_2	CaO	SiO_2
a	10·0	5·0	5·0	37·9	42·1	5·9	7·5	3·75	40·7	42·1
b	12·5	4·9	4·9	36·8	40·9	7·5	7·4	3·7	40·0	41·5
c	15·0	4·7	4·7	35·8	39·8	9·05	7·2	3·6	39·3	40·8
d	17·5	4·6	4·6	34·7	38·6	10·75	7·1	3·6	38·7	40·2
e	20·0	4·45	4·45	33·7	37·4	12·3	6·9	3·4	38·0	39·4
f	22·5	4·3	4·3	32·7	36·3	14·0	6·8	3·3	37·2	38·6
g	25·0	4·1	4·1	31·6	35·1	15·85	6·55	3·3	36·4	37·9
h	10·0	5·0	5·0	43·5	36·5	5·9	7·5	3·7	46·5	36·5
i	12·5	4·9	4·9	45·3	32·4	7·5	7·4	3·7	48·9	32·6
j	15·0	4·7	4·7	45·4	30·2	9·0	7·1	3·6	49·6	30·8
k	17·5	4·5	4·5	44·1	29·3	10·6	7·05	3·55	48·6	30·2
l	22·5	4·3	4·3	38·9	30·0	14·0	6·75	3·3	44·1	31·8
m	25·0	4·1	4·1	37·0	29·7	15·75	6·55	3·2	42·5	31·8

Table 7.

Of a large number of systems which were tried, the one which most nearly fitted the points, was the quinternary calcium metasilicate-anorthite-gehlenite-akermanite-$2CaO.TiO_2$. The quaternary calcium metasilicate-anorthite-akermanite-$2CaO.TiO_2$ of this system included the points a,b,c,d and e, of Table 6, while the quaternary calcium metasilicate-gehlenite-akermanite-$2CaO.TiO_2$, included the points h,i,j and k. To include the points f and g, it was necessary to introduce what would be the logically adjacent quinternary, namely, akermanite-anorthite-gehlenite-monticellite-$2CaO.TiO_2$. The points f and g, then approximated to the anorthite-akermanite-$2CaO.TiO_2$-monticellite quaternary. It was found impossible to fit the points l and m into any reasonable system.

As an indication of the method of balancing up the constituent oxides of the slags, the method as applied to the point d will be outlined in detail.

	Al_2O_3	MgO	TiO_2	CaO	SiO_2
Molecular composition of point d.	10.75	7.1	3.6	38.7	40.2
7.1% MgO if present as akermanite would take up:-	—	7.1	—	14.2	14.2
10.75% Al_2O_3 if present as anorthite would take up:-	10.75	—	—	10.75	21.5
3.6% TiO_2 if present as $2CaO.TiO_2$ would take up:-	—	—	3.6	7.2	—
This leaves:-	0	0	0	6.55	4.5

Table 8.

Thus, to use up all the residual lime and silica as calcium metasilicate, it is necessary to replace 1% of the lime by 1% silica. In other words, the composition of the minimum deviates from the proposed quaternary by + 1.0% lime. The deviations for the other points were calculated

were calculated/ in a similar manner and are summarised in Table 9. This table also gives the suggested constituent constitution of the eleven points.

No.	Molecular % of : — Calcium Metasilicate	Gehlenite	Anorthite	Akermanite	$2CaO.TiO_2$	Monticellite	Deviation as excess moles. % of:- CaO	SiO_2
a	27·6	0	23·6	37·5	11·2	0	0	1·5
b	22·0	0	30·0	37·0	11·1	0	0	0·7
c	17·0	0	36·2	36·0	10·8	0	0·2	0
d	11·0	0	43·0	35·5	10·8	0	1·0	0
e	6·0	0	49·2	34·5	10·2	0	2·0	0
f	0	0	56·0	33·0	9·9	1·0	3·0	0
g	0	0	63·4	17·5	9·9	9·0	3·9	0
h	28·0	23·6	0	37·5	11·1	0	0	1·6
i	22·0	30·0	0	37·0	11·1	0	0·7	0
j	17·8	36·0	0	35·5	10·8	0	1·3	0
k	11·8	42·4	0	35·2	10·7	0	0·3	0

Table 9.

According to the above theory, the only new mineral introduced into the melts by the presence of 5% titania, possesses the formula $2CaO.TiO_2$. The author has been unable to find any previous reference to this compound in the very fragmentary literature concerning the chemistry

the chemistry/ of lime and titania, although reference has been noted to the compound $CaO.TiO_2$. It must, therefore, be emphasised that until the existence of $2CaO.TiO_2$ is either proved or disproved, the quinternary calcium metasilicate-anorthite-gehlenite-akermanite-$2CaO.TiO_2$ must be regarded as no more than a suggestion.

SUMMARY of CONCLUSIONS.

(1) The investigation has yielded no indication of why titaniferous slags, containing no more than 5% titania, should be difficult to manage in the blast furnace.

(2) An addition of 5·3% magnesia decreases the viscosity of lime-alumina-silica slags of CaO/SiO_2 0·8 - 1·5 and 11·1% alumina. The effect is greatest in the slags of higher basicity.

(3) An addition of 5·0% titania generally increases the viscosity of lime-alumina-silica-magnesia slags of CaO/SiO_2 0·8 - 1·5 containing 10·5% alumina and 5·3% magnesia. At temperatures between 1450 and 1500°C, however, the titania bearing slags of CaO/SiO_2 1·2 - 1·5, are more fluid than the parent quaternary slags.

(4) The viscosity of the lime-alumina-silica-magnesia-titania slags examined is a complex function of the composition. An increase of lime or silica content may increase or decrease the viscosity at a given temperature, depending entirely on the slag composition. An increase of alumina content, generally increases viscosity.

(5) Minima in the isothermal curves of viscosity against composition of the lime-alumina-silica and lime-alumina-silica-magnesia slags, have been attributed to changes of mineral constitution. A system of mineral constituents has been proposed to explain minima in the corresponding isothermal curves of the lime-alumina-silica-magnesia-titania slags.

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